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LESSONS

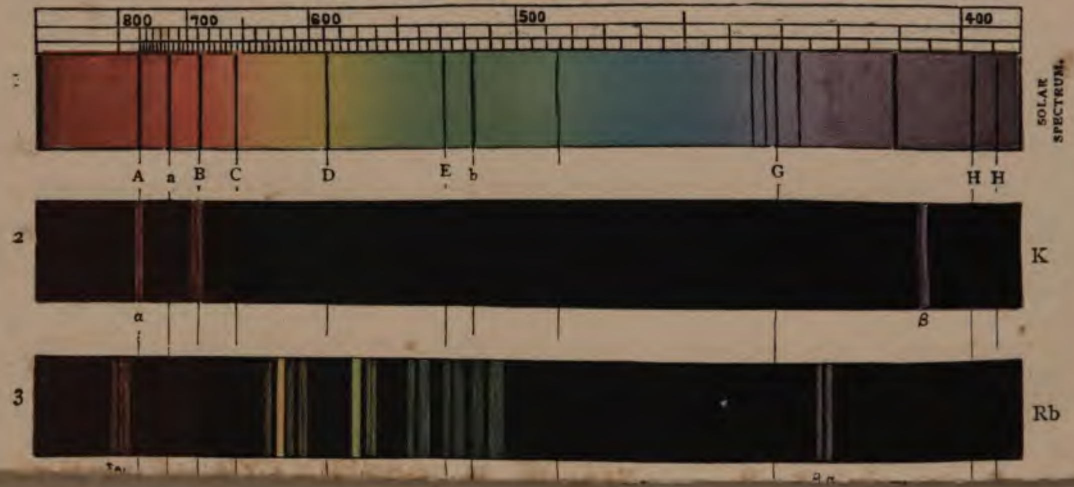
IN

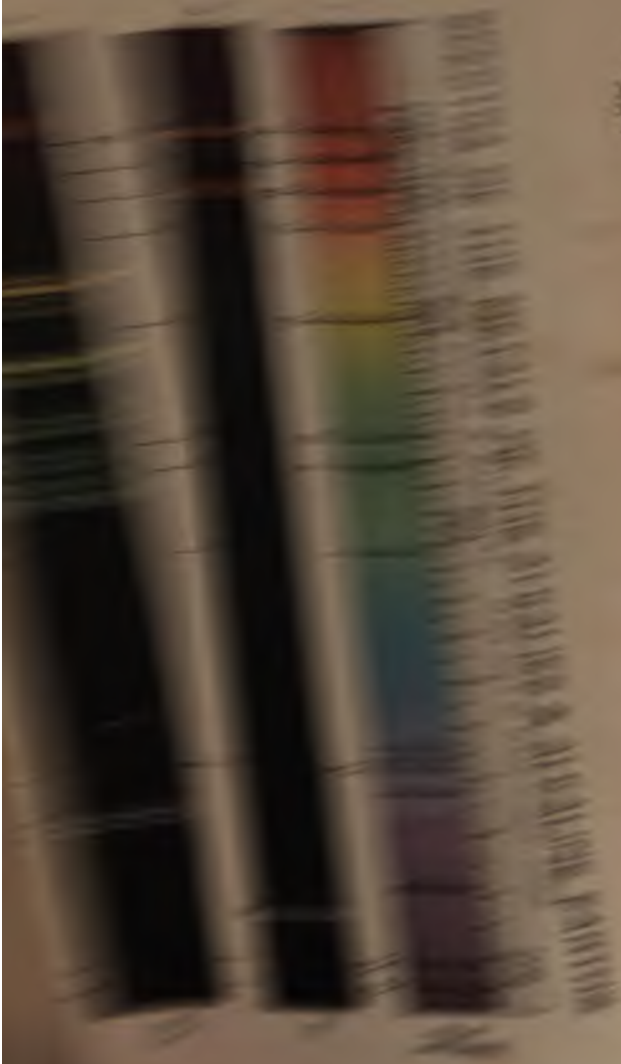
ELEMENTARY CHEMISTRY

INORGANIC AND ORGANIC

SPECTRA OF THE METALS OF THE ALKALIES & ALKALINE EARTHS.

From the Drawings of BUNSEN & KIRCHHOFF. *With Scale of Wave-Lengths added.*





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LESSONS

IN

ELEMENTARY CHEMISTRY

3447

INORGANIC AND ORGANIC

BY

SIR HENRY E. ROSCOE, LL.D., F.R.S.

LATE PROFESSOR OF CHEMISTRY IN THE VICTORIA UNIVERSITY, THE OWENS
COLLEGE, MANCHESTER

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PREFACE

IN the following pages I have endeavoured to arrange the most important facts and principles of Modern Chemistry in a plain but precise and scientific form, suited to the present requirements of Elementary Instruction.

For the purpose of facilitating the attainment of that exactitude in the knowledge of the subject, without which the introduction of physical science into the school system is worse than useless, I have added a series of Exercises and Questions upon the Lessons. The pupil must learn to work out accurately both the numerical and descriptive examples, and the teacher may find it advisable to add largely to their number. Particular attention should be given to the calculation of the relations between the weights of gases, and their volumes measured under varying circumstances of temperature and pressure.

The metric system of weights and measures and the centigrade thermometric scale are used throughout the work.

I have much pleasure in thanking my friend, Mr. Schorlemmer, for the aid which he has given me, especially in revising the proofs; and I have also to acknowledge the

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care and attention bestowed on the woodcuts and on the chromolithographic frontispiece by Mr. J. D. Cooper and Mr. Collings.

H. E. R.

MANCHESTER, *Jan.* 1869.

IN the present wholly revised Edition several changes of importance have been made, especially as regards the arrangement of the Organic portion of the work, which will, I trust, simplify the study of this branch of the Science. In addition to this change of form I have endeavoured to keep the book up to the level of the Science of the day by inserting the most important discoveries which have been made during the last four years.

H. E. R.

MANCHESTER, *Oct.* 1875.

I HAVE, in the present Edition, amongst other alterations and additions adopted for the combining weights of the elements, numbers derived from Stas's accurate experiments, oxygen being taken at 15·96 instead of 16. In many instances these numbers do not greatly differ from those formerly used, and in ordinary calculations the older numbers may, for the sake of simplicity, still be employed.

H. E. R.

Oct. 1877.

THE progress of Chemistry is now so rapid, that revisions of text-books in which the newest facts and most accurate data are to be given, must frequently be made. In this Edition, wholly reprinted, I have endeavoured to place before the student all the important additions to the Science which have been made since the last reprint. In the Organic portion of the work, the necessary changes and additions are of greater extent than those in the less progressive Inorganic department of the Science.

H. E. R.

July, 1885.

WHAT is said in the Preface to the new Edition of 1885 applies with equal or even with greater force to this new Edition of 1892. If a text-book of Chemistry is to represent the condition of the Science of the day—that is to be in reality what it professes to be—it must be frequently revised, and even re-written. Whilst keeping as far as possible within the desirable limits of such a little book, I have, in this Edition, endeavoured not only to introduce all the more important discoveries of the last six years, but to make improvements throughout the work which I hope will be to the benefit of my readers.

My thanks are due to my friend Dr. H. G. Colman for the great assistance which he has given me in passing this Edition through the press.

H. E. R.

February, 1892.

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INTRODUCTION

LESSON I

By *chemical action* we signify that which occurs when two or more substances so act upon one another as to produce a third substance differing altogether from the original ones in properties ; or when one substance is brought under such conditions that it forms two or more bodies differing from the original one in properties. Thus, if powdered sulphur and fine copper-filings be well mixed together, the colour of the sulphur as well as that of the copper will disappear, and to the unaided eye the mixture presents a uniform greenish tint ; by the help of the microscope, however, the particles of copper may be seen lying by the side of the particles of sulphur ; and we can wash away the lighter sulphur with water, leaving the heavier copper behind. Here *no chemical action* has occurred ; the sulphur and copper were only *mechanically mixed.* If we next gently heat some of the mixture we see that it soon begins to glow, and on examining the mass we notice that both the copper and the sulphur have disappeared as such, that they cannot be distinguished even by the most powerful microscope, and that in their place we have formed a black substance possessing properties entirely different from those possessed either by the copper or by the sulphur. Here a *chemical change* has occurred ; the copper and the sulphur are said to have *combined chemically* to form a *compound* out of which these two substances can be regained in exactly the quantities used.

In like manner, when a candle burns in the air a chemical change is going on ; and although the candle gradually disappears, the materials of which it is made up are not destroyed or lost; they simply pass into a state in which they are invisible to our eyes, but their presence may be ascertained by other means. Thus, if we burn a candle for a few minutes in a clean bottle filled with air, and afterwards pour in some clear lime-water, we shall notice that the liquid, which remains clear in pure air, becomes at once milky, showing the presence of an invisible gaseous body produced by the burning of the candle, which possesses properties different from those of pure air. Although an apparent loss of matter occurs when a candle burns, it is easy to show by a simple experiment not only that this is not the case, but that, on the contrary, an increase of weight has occurred; this increase is occasioned by the constituent parts of the tallow or wax having united chemically with an invisible gas (called oxygen) present in the air. For this purpose a piece of glass tubing (A, Fig. 1), ¾ inch wide and 10 inches long, is closed at each end with a cork; through the upper cork a bent glass tube passes, whilst through the lower one several holes are bored, and into one of these a small taper is fastened. A bent tube (B, Fig. 1), filled with pieces of caustic soda, is attached by a perforated cork, as seen in the figure, and the apparatus thus arranged is hung at the end of one arm of a pair of scales, and exactly counterpoised by weights placed in the pan on the other arm. The end of the tube (C) is now attached, by means of a piece of vulcanised caoutchouc tubing, to an opening at the top of a vessel filled with water and furnished at the bottom with a tap through which the water can flow out; as the water flows out on opening this tap, air must pass in to supply its place through the whole apparatus by the holes in the perforated cork. This cork is then removed, the taper lighted, and the cork and taper

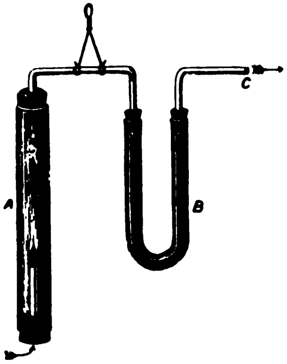

FIG. 1.

quickly replaced; after the candle has burnt for three or four minutes, the vulcanised tubing is disconnected, and the glass tube allowed to hang freely. It is then seen that the weight of the apparatus is greater than it was before the candle was burnt, the pieces of caustic soda having absorbed the substances (carbonic acid and water) produced by the combination of the constituents of the taper (carbon and hydrogen) with the oxygen of the air.

By the careful examination of all the known cases of chemical action it has been satisfactorily proved that a *loss* of matter never takes place, that ***matter is indestructible*** and that in chemical actions, such as that going on in the burning of the candle, a change of state and not an annihilation of matter occurs. The truth of this first great principle in chemical science has been gradually demonstrated by finding that the weights of the substance acting chemically upon one another always remain the same after as before the chemical changes have occurred. For determining very accurately the weight of substances, an instrument called the

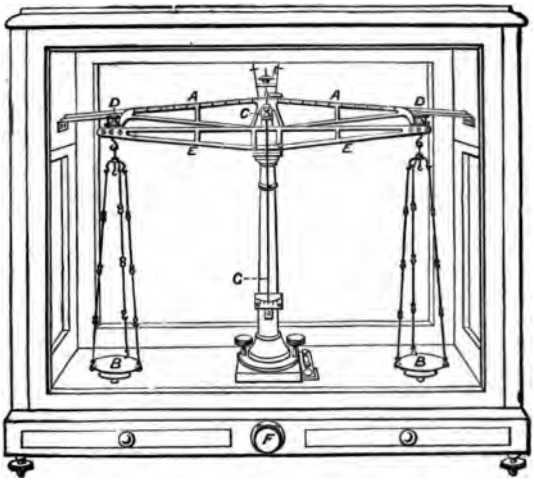

FIG. 2.

chemical balance is employed. Fig. 2 represents one form of chemical balance. It consists of a perforated brass beam (AA) vibrating about its centre, at which is fixed a triangular knife-edge of agate (C): this rests upon a horizontal agate plane attached to the upright brass pillar. To each end of the beam the light brass pans (BB) are attached, each pan being suspended by an agate plane upon an agate knife-edge fixed on the end of the beam at DD. This mode of rest and support is to render the amount of friction as small as possible, and thus to insure delicacy in the instrument. In order to prevent the agate edges from being spoilt by constant wear on the agate planes, the beams and the ends (DD) are supported by the brass arm (EE) when the balance is not in use, so that the agate surfaces do not touch ; the beam and pans are released when required by turning the handle F. The substance to be weighed is placed in one pan, and weights added one by one to the other until the instrument is in equilibrium ; this is ascertained by the long pointer (G) vibrating to an equal distance on each side of the central mark. A balance such as that represented in the figure will turn with $\frac{1}{10}$ of a milligram when loaded with 100 grams (see p. 24), or will indicate with this load the one-millionth part of the substance weighed.

The *stability* of the balance is insured by the centre of gravity being situated below the point or axis of suspension. The *sensibility* of the balance is secured by having the beam as light and as long as is possible consistently with rigidity, and by having the distance between the centre of gravity and the point of suspension as small as possible, also by reducing the friction on all the parts to a minimum. The *accuracy* of the balance depends upon having the two arms of equal length. All delicate chemical balances are kept in glass cases to avoid draughts of air, which would disturb the accuracy of the weighings, as well as to protect the instrument against dust and moisture.

The aim of the chemist is to examine the properties of all substances with regard to their actions upon one another in producing bodies essentially differing from the originals. In order thoroughly to carry out his purpose he is obliged to resort to *experiment;* that is, he has to place the substances which he is examining under circumstances, perhaps not found in nature, which he can control and vary. Hence chemistry is called an *experimental science.* In thus investigating all the materials within his reach, whether solid, liquid, or gaseous, whether contained in the earth, sea, or air; whether belonging to the animal or to the vegetable creation, the chemist finds himself able to divide substances into two great classes: (1) COMPOUND SUBSTANCES—those which he can split up into two or more essentially different materials: and (2) ELEMENTS or SIMPLE SUBSTANCES—those which he has not been able thus to split up, and out of which nothing essentially different from the original substances has been obtained.

Compound bodies are made up of two or more elementary substances chemically combined with each other: thus sulphur and copper are elementary bodies: out of each of these nothing different from sulphur or copper can be obtained; whereas, when the two bodies are heated together, a compound is formed from which both of the original elementary constituents can at any time be prepared. Water is a compound body—it can be split up into two elementary gases, hydrogen and oxygen; common salt, again, is a compound of a gas (chlorine) with a metal (sodium); and limestone, clay, sugar, and wax may also serve as examples of compound bodies: whilst phosphorus, charcoal, iron, mercury, and gold may be mentioned as belonging to the class of simple substances. The following experiment well illustrates the decomposition of a compound into two simple substances. A small quantity of the red powder called mercury oxide is introduced into a test-tube, and heated in a gas flame; when hot, the oxide gradually decomposes, a grey deposit of metallic mercury in small globules collect upon the cooler parts of the glass, whilst the tube becomes filled with colourless oxygen gas, whose presence can be demonstrated by the rekindling of a glowing chip of wood plunged into the tube. On continued heating the whole of the red powder is found to be split up into the two elements, mercury and oxygen, which together weigh exactly as much as the red oxide from which they were obtained.

The *elementary bodies*, for the sake of convenience, are arbitrarily divided into two classes, the *metals* and the *non-metals.* In the first are placed elements such as gold, iron,

lead, mercury, tin ; in the second, those elements which are gases at the ordinary temperature, such as oxygen, hydrogen, &c., together with some solid elements, as sulphur, charcoal, &c. The number of the metals is much larger than that of the non-metals ; we are acquainted with at least fifty-three metals, and with only fifteen non-metals. These sixty-eight elements constitute the material out of which the whole fabric of the science is built ; every description of matter which has been examined is made up of these elements, either combined together to form compounds or in the uncombined or free state.

The science of chemistry has for its aim the experimental examination of the properties of the elements and their compounds, and the investigation of the laws which regulate their combination one with another. The applications of the principles of chemical science to the arts and manufactures are of the highest importance and interest ; they have exerted a most material influence upon the progress of civilisation, and have greatly tended to the elevation and benefit of mankind ; the instances are innumerable in which altogether new branches of industry have sprung up from the happy application of simple chemical principles, and there is scarcely an article in common use in the production of which some application of chemistry has not proved of essential value.

The following is a complete list of the elementary bodies known at present (1891). The names printed in large capital italics, as *BORON*, are the non-metals ; those in small roman capitals, as ALUMINIUM, are the more commonly occurring metals ; those in small type, as Caesium are the rarer metals.

Names.	*Symbols.*	*Combining Weights.*[1]
ALUMINIUM	Al	27·0
ANTIMONY	Sb	120·0
ARSENIC	As	74·9
BARIUM	Ba	136·8
Beryllium	Be	9·02
BISMUTH	Bi	208·4
BORON	B	11·0
BROMINE	Br	79·75
CADMIUM	Cd	111·9

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[1] For an explanation of the numbers see page 14.

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CARBON	C	11·97
Cerium	Ce	139·9
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CHROMIUM	Cr	52·0
COBALT	Co	58·6
COPPER	Cu	63·1
Didymium	D	142·0
Erbium	E	166·0
FLUORINE	F	19·1
Gallium	G	69·8
Germanium	Ge	72·75
GOLD	Au	196·7
HYDROGEN	H	1·0
Indium	In	113·4
IODINE	I	126·53
Iridium	Ir	192·7
IRON	Fe	55·9
Lanthanum	La	138·0
LEAD	Pb	206·4
Lithium	Li	7·01
MAGNESIUM	Mg	24·3
MANGANESE	Mn	55·0
MERCURY	Hg	199·8
Molybdenum	Mo	95·8
NICKEL	Ni	58·6
Niobium	Nb	94·0
NITROGEN	N	14·01
Osmium	Os	190·3
OXYGEN	O	15·96
Palladium	Pd	106·2
PHOSPHORUS	P	30·96
PLATINUM	Pt	194·5
POTASSIUM	K	39·04
Rhodium	Rh	104·1
Rubidium	Rb	85·2
Ruthenium	Ru	103·5
Scandium	Sc	44·0
SELENIUM	Se	78·0
SILVER	Ag	107·66
SILICON	Si	28·0
SODIUM	Na	22·99
STRONTIUM	Sr	87·2
SULPHUR	S	31·98
Tantalum	Ta	182·0
TELLURIUM	Te	125·0
Terbium	Tb	148·5
Thallium	Tl	203·6

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Erbium	E	166·0
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Niobium	Nb	94·0
NITROGEN	N	14·01
Osmium	Os	190·3
OXYGEN	O	15·96
Palladium	Pd	106·2
PHOSPHORUS	P	30·96
PLATINUM	Pt	194·5
POTASSIUM	K	39·04
Rhodium	Rh	104·1
Rubidium	Rb	85·2
Ruthenium	Ru	103·5
Scandium	Sc	44·0
SELENIUM	Se	78·0
SILVER	Ag	107·66
SILICON	Si	28·0
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IODINE	I	126·53
Iridium	Ir	192·7
IRON	Fe	55·9
Lanthanum	La	138·0
LEAD	Pb	206·4
Lithium	Li	7·01
MAGNESIUM	Mg	24·3
MANGANESE	Mn	55·0
MERCURY	Hg	199·8
Molybdenum	Mo	95·8
NICKEL	Ni	58·6
Niobium	Nb	94·0
NITROGEN	N	14·01
Osmium	Os	190·3
OXYGEN	O	15·96
Palladium	Pd	106·2
PHOSPHORUS	P	30·96
PLATINUM	Pt	194·5
POTASSIUM	K	39·04
Rhodium	Rh	104·1
Rubidium	Rb	85·2
Ruthenium	Ru	103·5
Scandium	Sc	44·0
SELENIUM	Se	78·0
SILVER	Ag	107·66
SILICON	Si	28·0
SODIUM	Na	22·99
STRONTIUM	Sr	87·2
SULPHUR	S	31·98
Tantalum	Ta	182·0
TELLURIUM	Te	125·0
Terbium	Tb	148·5
Thallium	Tl	203·6

Names.	*Symbols.*	*Combining Weights.*
Thorium	Th	231·5
TIN	Sn	117·8
Titanium	Ti	48·0
Tungsten	W	184·0
Uranium	U	239·0
Vanadium	V	51·2
Ytterbium	Yb	173·2
Yttrium	Y	89·0
ZINC	Zn	65·1
Zirconium	Zr	90·4

In addition to the elements above enumerated, a number of other bodies supposed to be elements have been stated to exist. They have not yet, however, been sufficiently characterised to make such existence certain. The names of some of these are Decipium, Holmium, Idumium, Norwegium, and Samarium.

Certain of the elements are very abundant, and occur widely distributed, whilst others have only been found in such minute quantities, and in such rare fragments, that their properties have not yet been fully studied. Thus, for instance, oxygen occurs throughout the air, sea, and solid earth, in such quantities as to make up nearly half the total weight of the earth whereas the compounds of yttrium, erbium, indium, &c., have only as yet been met with in very minute quantities.

The elements are distributed very irregularly throughout our planet: only four occur in the air, some thirty have been found in the sea; whilst all the known elements occur variously dispersed in the solid mass of the earth. The following table, giving the composition by weight of the primary rocks, shows that by far the greater part of the earth's solid body is made up of only eight elements, the remainder being found in much smaller quantities :—

Composition of the Earth's Solid Crust in 100 parts by Weight.

Oxygen	44·0 to 48·7	Calcium	6·6 to 0·9
Silicon	22·8 ,, 36·2	Magnesium	2·7 ,, 0·1
Aluminium	9·9 ,, 6·1	Sodium	2·4 ,, 2·5
Iron	9·6 ,, 2·4	Potassium	1·7 ,, 3·1

Doubtless other elements exist undiscovered in the earth in addition to those now known, for we find that where, with the progress of science, new and more accurate methods of examining the composition of matter have been employed, the existence of new elements has frequently been brought to light; thus within the last thirty years, several new elements have been discovered by the help of the method of Spectrum Analysis. Whether any of the bodies now termed elementary may, by the application of more powerful means than we at present possess, at some future time be split up into simpler constituents, is a question which we cannot answer with certainty. Judging, however, from precedent, we may consider the occurrence of such a thing as possible, or even likely; for the alkalis potash and soda were believed to be elements until the year 1807, when Sir H. Davy proved that they were in reality compounds.

Our knowledge of the chemical composition of the heavenly bodies was restricted, until lately, to that gained from the examination of those masses which fall on the earth's surface from an extra-terrestrial source, and known as meteorites, in which no element has been found which is not known in the earth. The foundations of a solar and stellar chemistry have, however, now been laid, and we are able to ascertain the presence of many well-known chemical substances in the sun and far distant fixed stars with as great exactitude and certainty as we are able to prove their presence in terrestrial matter (see p. 271).

LESSON II.

NON-METALLIC ELEMENTS.

IN the present work we shall consider the properties of the Non-metals and their compounds in the following order:—

OXYGEN.
HYDROGEN.
NITROGEN.
CARBON.
CHLORINE.
BROMINE.
IODINE.
FLUORINE.
SULPHUR.
SELENIUM.
TELLURIUM.
SILICON.
BORON.
PHOSPHORUS.
ARSENIC.

Names.	*Symbols.*	*Combining Weights.*
Thorium	Th	231·5
TIN	Sn	117·8
Titanium	Ti	48·0
Tungsten	W	184·0
Uranium	U	239·0
Vanadium	V	51·2
Ytterbium	Yb	173·2
Yttrium	Y	89·0
ZINC	Zn	65·1
Zirconium	Zr	90·4

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Hydrogen.
Nitrogen.
Carbon.
Chlorine.
Bromine.
Iodine.
Fluorine.
Sulphur.
Selenium.
Tellurium.
Silicon.
Boron.
Phosphorus.
Arsenic.

lead, mercury, tin; in the second, those elements which are gases at the ordinary temperature, such as oxygen, hydrogen, &c., together with some solid elements, as sulphur, charcoal, &c. The number of the metals is much larger than that of the non-metals; we are acquainted with at least fifty-three metals, and with only fifteen non-metals. These sixty-eight elements constitute the material out of which the whole fabric of the science is built; every description of matter which has been examined is made up of these elements, either combined together to form compounds or in the uncombined or free state.

The science of chemistry has for its aim the experimental examination of the properties of the elements and their compounds, and the investigation of the laws which regulate their combination one with another. The applications of the principles of chemical science to the arts and manufactures are of the highest importance and interest; they have exerted a most material influence upon the progress of civilisation, and have greatly tended to the elevation and benefit of mankind; the instances are innumerable in which altogether new branches of industry have sprung up from the happy application of simple chemical principles, and there is scarcely an article in common use in the production of which some application of chemistry has not proved of essential value.

The following is a complete list of the elementary bodies known at present (1891). The names printed in large capital italics, as *BORON*, are the non-metals; those in small roman capitals, as ALUMINIUM, are the more commonly occurring metals; those in small type, as Caesium are the rarer metals.

Names.	*Symbols.*	*Combining Weights.*[1]
ALUMINIUM	Al	27·0
ANTIMONY	Sb	120·0
ARSENIC	As	74·9
BARIUM	Ba	136·8
Beryllium	Be	9·02
BISMUTH	Bi	208·4
BORON	B	11·0
BROMINE	Br	79·75
CADMIUM	Cd	111·9

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[1] For an explanation of the numbers see page 14.

Names.	*Symbols.*	*Combining Weights.*
Caesium	Cs	133·0
CALCIUM	Ca	39·9
CARBON	C	11·97
Cerium	Ce	139·9
CHLORINE	Cl	35·37
CHROMIUM	Cr	52·0
COBALT	Co	58·6
COPPER	Cu	63·1
Didymium	D	142·0
Erbium	E	166·0
FLUORINE	F	19·1
Gallium	G	69·8
Germanium	Ge	72·75
GOLD	Au	196·7
HYDROGEN	H	1·0
Indium	In	113·4
IODINE	I	126·53
Iridium	Ir	192·7
IRON	Fe	55·9
Lanthanum	La	138·0
LEAD	Pb	206·4
Lithium	Li	7·01
MAGNESIUM	Mg	24·3
MANGANESE	Mn	55·0
MERCURY	Hg	199·8
Molybdenum	Mo	95·8
NICKEL	Ni	58·6
Niobium	Nb	94·0
NITROGEN	N	14·01
Osmium	Os	190·3
OXYGEN	O	15·96
Palladium	Pd	106·2
PHOSPHORUS	P	30·96
PLATINUM	Pt	194·5
POTASSIUM	K	39·04
Rhodium	Rh	104·1
Rubidium	Rb	85·2
Ruthenium	Ru	103·5
Scandium	Sc	44·0
SELENIUM	Se	78·0
SILVER	Ag	107·66
SILICON	Si	28·0
SODIUM	Na	22·99
STRONTIUM	Sr	87·2
SULPHUR	S	31·98
Tantalum	Ta	182·0
TELLURIUM	Te	125·0
Terbium	Tb	148·5
Thallium	Tl	203·6

OXYGEN.

Symbol O, *Atomic weight* 15·96. *Density* 15·96.—Oxygen is a gaseous substance, and exists in the free state in the atmosphere, of which it constitutes about one-fifth by bulk, whilst, in combination with the other elements, it forms nearly half the weight of the solid earth, and eight-ninths by weight of water. Oxygen was discovered in the year 1774 by Priestley in England, and independently in 1775 by Scheele in Sweden.

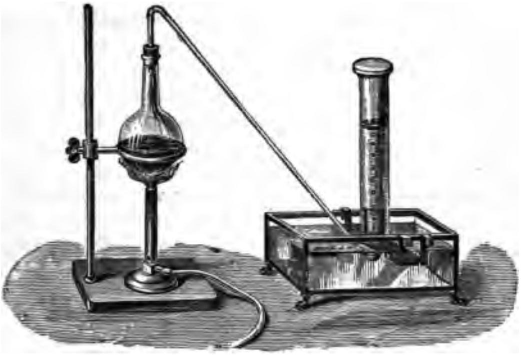

FIG. 3.

Priestley prepared oxygen gas by heating red mercuric oxide to a high temperature, this compound being itself obtained by heating mercury in the air for some time at a temperature a little below that at which it boils. Mercuric oxide has been shown by experiment always to consist of 200 parts by weight of mercury, and sixteen parts by weight of oxygen; when strongly heated, it is decomposed, and yields metallic mercury and oxygen gas.

Oxygen can be more cheaply obtained by heating potassium chlorate (commonly called chlorate of potash), a white salt which yields on heating 39·2 per cent. of its weight of this gas. In order to collect the oxygen thus given off, powdered potassium chlorate is placed in a small thin glass flask, furnished with a well-fitting cork, into which a bent tube is inserted. The lower end of the tube dips under the surface of water in a *pneumatic trough*, and the gas, on being evolved, bubbles out from the end of the tube, and rises into jars or bottles placed with their mouths downwards in the trough, filled with water which the gas displaces. Fig. 3 shows the arrangement of the apparatus needed for the preparation of oxygen gas. If a small quantity of manganese dioxide (black oxide of manganese) be mixed with the potassium chlorate, the oxygen is given off from the chlorate at a much lower temperature. The manner in which the manganese dioxide acts is not known, as it is found unaltered at the end of the operation. Many other oxides have a similar action.

Oxygen is a colourless inodorous gas, which when subjected to a pressure of 320 atmospheres at — 140° condenses to a liquid which is colourless in thin layers, but in layers 30mm. thick has a sky-blue colour, and boils at – 184·7°. The specific gravity of liquid oxygen is 0·8737 compared with water, whilst that of the gas is 15·96 compared with hydrogen (the lightest gas known), and 1·1056 compared with air. One litre of oxygen gas at 0° C., under 760 mm. pressure weighs 1·4298 grams.

All the elements, with the single exception of fluorine, combine with oxygen to form *oxides*. In this act of combination, which is termed *oxidation*, heat is always, and light is frequently, given off. When bodies unite with oxygen, evolving light and heat, they are said to *burn*, or *undergo combustion*. All bodies which burn in the air burn with increased brilliancy in oxygen gas; and many substances, such as iron, which do not readily burn in the air, may be made to do so in oxygen. A red-hot chip of wood, or a taper with glowing wick, is suddenly rekindled and bursts into flame when plunged into a jar of this gas. Sulphur, which in the air burns with a pale lambent flame, emits in oxygen a bright violet light; and a small piece of phosphorus, when inflamed and placed in oxygen, burns with a dazzling light. If the jars in which these experiments have been performed be afterwards examined, it is found that the substances produced by combustion of sulphur and phosphorus

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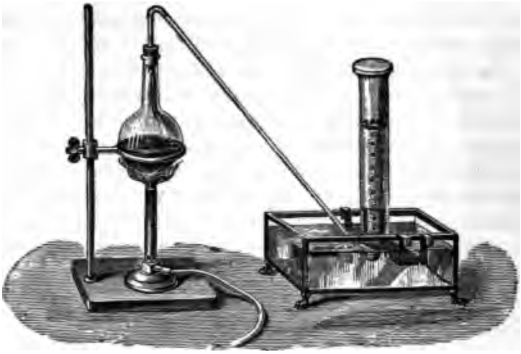

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The true explanation of the part played by the oxygen of the air when substances burn, or undergo combustion, was first put forward by Lavoisier in Paris in 1778. The explanation thus given forms the foundation of all the present ideas regarding elements, compounds, chemical action, &c., so that the discovery of oxygen may be looked upon as marking the birth of modern chemistry.

Many other substances may be employed for the preparation of oxygen ; thus, if large quantities of the gas are needed, manganese dioxide (a substance of frequent occurrence in nature) may be heated to redness in an iron bottle ; 100 parts by weight of the oxide yield 12·3 by weight of oxygen. Oxygen is also now prepared on the large scale direct from the air. The process employed depends upon the fact that barium oxide (p. 207) when heated in the air at a moderate temperature takes up more oxygen forming barium dioxide; the latter, when more strongly heated is reconverted into barium oxide and oxygen gas, which is then compressed by means of pumps into strong wrought-iron bottles. Other methods which have been proposed for manufacturing oxygen on the large scale will be mentioned under bleaching powder, and sulphuric acid (see pp. 128, 205).

Another interesting decomposition by which oxygen is set free is that effected by sunlight upon the carbonic acid gas contained in the air ; this is accomplished by means of the green colouring matter of plants. Sunlight has the power, in presence of this green colouring matter, of decomposing carbonic acid ; the carbon is taken up by the plant for its growth, whilst the oxygen is set free, and is afterwards used by animals for the support of the process of respiration. In the act of inspiration (filling the lungs) animals breathe in the oxygen of the air, whilst in that of expiration (emptying the lungs) they breathe out carbonic acid gas. Hence oxygen is necessary to animal life, wherefore this gas was formerly termed *vital air*. The chemical change which oxygen effects upon the body of the animal is in fact identical with that which goes on when a piece of charcoal burns in the air or oxygen; this may be rendered evident by a simple experiment. If some clear lime-water be poured into a bottle of oxygen in which charcoal has been burnt, the lime-water will become milky, owing to the formation of a compound of lime and carbonic acid (called chalk), this acid being produced by the combustion: if the air contained in the lungs be next blown through a piece of glass tubing into some more clear lime-water, a turbidity (from the formation of chalk) will at once occur, proving that carbonic acid gas is given off from the lungs. This carbonic acid arises from the oxidation of the constituents of the animal body, and by this oxidation the heat of the body, which is greater than that of surrounding inanimate objects, is sustained. When this chemical process stops the animal dies, and the temperature of the body sinks to that of the neighbouring objects. Carbonic acid, nitrogen, and some other gases cause death when inhaled, because they do not contain free oxygen, and hence the process of oxidation in the body ceases. This cause of death is independent of any poisonous action of the gases.

COMPOSITION OF SUBSTANCES—CHEMICAL SYMBOLS.

When the composition of a substance is determined by resolving the compound into its elementary constituents, a *chemical analysis* of that substance is said to have been made; and if the proportions by weight in which each of the constituents is present be determined, a *quantitative* analysis of the substance has been made. When the composition is ascertained by bringing the constituent parts together, we are said to determine the composition by *synthesis*. If we analyse potassium chlorate we find that, from whatever source this salt may be derived, it always possesses the same unalterable composition. This is true of every definite chemical compound; indeed, were it not so, chemistry as a science could not exist. Potassium chlorate is made up of three elementary bodies, chlorine, potassium, and oxygen, combined together in the following proportions by weight :

Chlorine	35·37	parts by weight.
Potassium	39·04	,,
Oxygen	47·88	,,
Potassium Chlorate .	122·29	,,

When the salt is heated, the whole of the oxygen comes off as gas : 122·29 parts yield 47·88 parts of oxygen, while 74·41 parts of a white solid compound of chlorine and potassium, called *potassium chloride*, remain behind. Hence the weight of oxygen which can be obtained from any given weight of potassium chlorate, and *vice versâ* can be calculated.

In order to express the composition of substances more conveniently than can be done by writing the names of the elementary constituents at full length, chemists use a kind of short-hand, or symbolic language, some of the principles of which must now be shortly explained. Instead of writing the whole name, the first letter or the first two letters of the name alone are employed to designate the element ; sometimes using the Latin or Greek name. Thus Cl stands for Chlorine, O for Oxygen, and K (from Kali, another name for Potash) for Potassium.

These letters, however, signify more than this ; they stand not only for the elements in question, but they all have certain numbers belonging to them which indicate the proportions by weight in which the several elements are found by experiment to combine with each other. Thus Cl does not merely express the name of the substance, chlorine, nor does it stand for any indefinite quantity of it ; nor, again, does Cl mean any absolute weight of chlorine expressed in pounds, ounces, or grains. It does, however, denote that the smallest quantity by weight of chlorine which can enter into chemical combination is exactly 35·37 times as great as the smallest quantity of hydrogen (H), which also enters into combination. So that the symbol HCl means that a substance, called hydrochloric acid, contains 35·37 times as much chlorine by weight as it contains hydrogen, this latter being represented as the unit. In like manner K always has the combining proportion of 39·04 and O of 15·96. Hence it is evident that we may express by symbols not only the *qualitative* but also the *quantitative* composition of chemical substances. Thus, potassium chlorate consists of

Potassium	39·04	or K.
Chlorine	35·37	,, Cl.
Oxygen	47·88 = 3 × 15·96	,, O_3.

The symbol of potassium chlorate is, therefore, $KClO_3$: the juxtaposition of the letters signifies that the elements are combined together in the proportions by weight indicated by the respective letters ; the figure 3 placed below the letter O shows that the combining weight of oxygen (15·96) is to be taken three times. The sum of the combining weights (in this case 122·29) of the elementary constituents is called the combining weight of the compound. In like manner each of the elements has its particular symbol and number attached, signifying the proportion by weight in which it combines (see Table, pp. 6-8). The reasons which have led chemists to adopt these special numbers for the *combining weights* or *proportions* of the elements, each of which has been determined by careful experiment, and the laws which have been found to regulate their combination, will be explained as our stock of chemical facts gradually becomes larger.[1]

On casting the eye down the column of combining weights on pp. 6, 7, and 8, it will be seen that many of these numbers approach nearly to whole numbers:

Thus	Oxygen	15·96	is nearly	16.
,,	Sulphur.	31·98	,,	32.
,,	Carbon	11·97	,,	12.
,,	Nitrogen	14·01	,,	14.
,,	Mercury	199·8	,,	200.
,,	Zinc	64·9	,,	65.

&c., &c.

For calculations in which no very great degree of exactitude is needed, it will suffice to employ the simpler whole numbers, when the exact combining weight, as given in the table, approaches within narrow limits of a whole number. In the following pages the calculations have usually been thus made. In cases in which accuracy is requisite, the exact weights as given in the table must of course be employed. An example of this latter kind is given on p. 29.

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[1] These combining weights or proportions are usually called *atomic weights*. The meaning of this term is explained on p. 57.

OZONE.

Pure oxygen undergoes a remarkable modification when a series of electric discharges is passed through the gas : it thus attains more active properties ; it possesses a peculiar smell, and is able to set free iodine from potassium iodide, as well as to effect oxidations which common oxygen is unable to bring about. This *allotropic* (ἄλλος, another, τρόπος, form) modification of oxygen has been termed *Ozone*. If a series of silent electric discharges be passed through pure oxygen, the gas becomes diminished in volume by about one-twelfth, and is partly transformed into ozone : it has not yet been found possible thus to convert the whole of the oxygen into ozone. If however a substance be present, such as potassium iodide, capable of absorbing the ozone as it is formed, the whole of the oxygen can be transformed into this active modification. The peculiar smell which is observed when an electrical machine is worked is caused by the presence of ozone ; and if a paper, dipped in a solution of potassium iodide and starch paste, be held opposite a point on the conductor of the machine, the paper becomes blue owing to the liberation of iodine and the formation of a blue compound of iodine and starch. Ozone can be obtained in several other ways ; it is formed when a stick of phosphorus is allowed to hang in a bottle filled with moist air ; it is produced in small quantities in the electrolytic decomposition of water (see p. 34) ; and it is formed by the action of strong sulphuric acid upon a salt called potassium permanganate.

The amount of condensation which common oxygen undergoes, as well as the quantity of ozone formed, being known, the density of ozone can be ascertained. It is found that ozone is 1½ times as heavy as oxygen ; that is, 3 volumes of oxygen condense to form 2 volumes of ozone. Ozone has been liquefied by exposure to high pressure and great cold, the liquid having an indigo blue colour. When ozone is passed through a moderately heated tube it is decomposed into ordinary oxygen. This serves to distinguish it from other gases which produce the same oxidising effect, such as the oxides of nitrogen, which are not thus decomposed, and also from hydrogen dioxide, which under these circumstances yields water and oxygen.

Ozone exists in the atmosphere, and its presence is recognized by the blue colour which it imparts to paper impregnated with starch paste and iodide of potassium solution. It is not found in the air of towns or inhabited spaces, as it is decomposed by the organic matter present in such air.

HYDROGEN.

Symbol H. *Atomic Weight* 1. *Density* 1.—Hydrogen is a colourless invisible gas, possessing neither taste nor smell ; it is the lightest body known, being 14·43 times lighter than air. It occurs free in small proportions in certain volcanic gases, and it has been shown to exist absorbed in certain specimens of meteoric iron ; but it is found in much larger quantities, combined with oxygen to form water (ὕδωρ, water, and γεννάω, I produce), and it is by the decomposition of water, or of some other similar hydrogen compound, that the gas is always prepared. Hydrogen appears to have been first obtained by Paracelsus in the sixteenth century, but its properties were first exactly studied by Cavendish in 1781. One-ninth of the weight of water consists of hydrogen, and this gas can readily be obtained from it by the action of certain metals which decompose the water, combining with the oxygen to form a metallic oxide, and liberating the hydrogen as a gas. The metals of the alkalis, potassium and sodium, decompose water at the ordinary temperature of the air ; some other metals, as iron, are only able to do so at a red heat ;

whilst others, for instance silver and gold, are unable to decompose water at all. When a small piece of potassium is thrown into water, an instantaneous decomposition of the water ensues, potassium hydroxide (caustic potash) is formed, and the hydrogen of the water is liberated, so much heat being at the same time evolved that the hydrogen takes fire and burns. If the potassium, or, still better, sodium, be wrapped in a piece of wire gauze, as shown in Fig. 4, and thus held below the surface of the water of the pneumatic trough, under the mouth of a cylinder, the hydrogen gas thus liberated may be collected, and its properties examined.

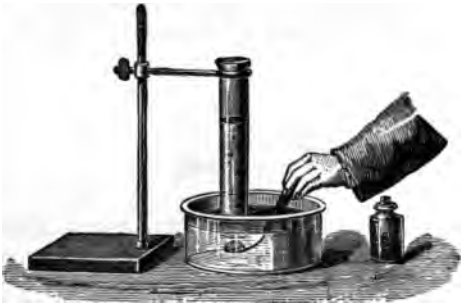

FIG. 4.

Water consists of 2 parts by weight of hydrogen and 15·96 parts by weight of oxygen, and its chemical symbol is therefore H_2O. When potassium or sodium acts upon water, half the hydrogen is liberated, the metal taking its place; this reaction can be represented by a *chemical equation*, as follows :—

$$H_2O + K = KHO + H,^1$$

or water and potassium yield potassium hydroxide and hydrogen. This equation shows us that for every 1 part by weight of hydrogen which is liberated (H), 39 parts by weight

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[1] The sign + used in chemical equations signifies "and" or "together with."

of potassium (K) enter into combination, and, likewise, that the sum of the weights of the products obtained is equal to that of the materials taken. The hydroxide which is formed dissolves in the water, but its presence can easily be detected either by the peculiar caustic taste which the solution possesses (whence its name, caustic potash), or by its power of turning to a blue colour a solution of litmus which has been reddened by an acid.

To prepare hydrogen by the action of red-hot iron on water, a piece of wrought-iron gas-piping, filled with iron turnings, must be heated in a furnace (Fig. 5), and steam from a small flask or boiler passed over the red-hot metal through the tube; hydrogen gas is given off, and oxide of iron left in the tube. The most convenient process of preparing hydrogen in quantity, depends upon a property possessed by those metals, such as iron or zinc, which decompose water at a red-heat; namely, that these metals are able to evolve hydrogen from dilute acids at the ordinary temperature of the air. For the purpose of thus obtaining hydrogen, a flask or bottle is provided with a cork and tube as represented in Fig. 6, some zinc clippings are introduced, and a mixture of one part of sulphuric acid (a compound of sulphur, oxygen, and hydrogen) and eight parts of water poured in through the tube funnel. A rapid effer-

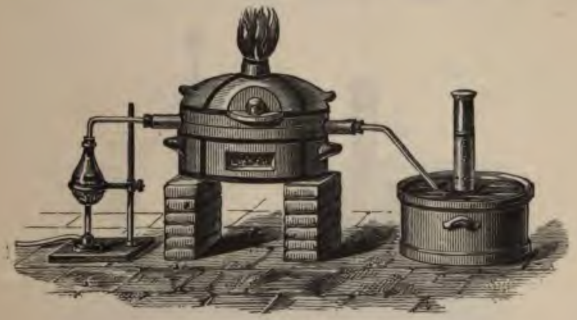

FIG. 5.

vescence soon commences, and the evolved gas is collected over water in bottles or cylinders as in the case of oxygen. Care must, however, be taken that all the air is expelled from the flask before the hydrogen is collected; this is easily ascertained to be the case by filling a test-tube with the gas, and trying whether the gas burns quietly when a lighted candle is brought to the mouth of the tube held downwards.

If we concentrate by boiling the liquid remaining in the flask after the evolution of the hydrogen, we find that white crystals separate out when the liquid cools: these consist of zinc sulphate. A given weight of zinc (with sulphuric acid and water) can always be made to produce a certain weight of hydrogen, and a certain weight of zinc sulphate will always be formed. It is found by experiment that 2 parts by weight of hydrogen can be obtained by dissolving 65 parts of zinc with the formation of 161 parts of zinc sulphate. This can be represented by the equation:

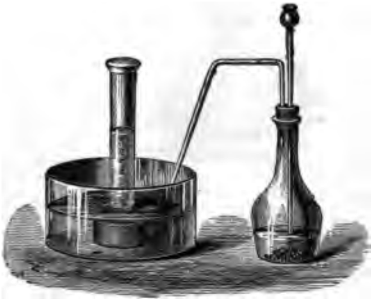

FIG. 6.

$$H_2SO_4 + Zn = ZnSO_4 + H_2,$$

which not only indicates that sulphuric acid and zinc yield zinc sulphate and hydrogen, but also informs us as to the weights of the respective substances taking part in the reaction; thus:

H_2 signifies 2×1 parts by weight of hydrogen,
S ,, 1×32 ,, ,, sulphur,
O_4 ,, $4 \times 16 = 64$,, ,, oxygen,

and H_2SO_4 signifies $2 + 32 + 64 = 98$ parts by weight of sulphuric acid. So the equation tells us that 98 parts by weight of sulphuric acid added to Zn or 65 parts by weight of zinc, yield $ZnSO_4$ or 161 parts by weight of zinc sulphate, and H_2 or 2 parts by weight of hydrogen.

Hydrogen burns in the air when a light is brought to it with a very slightly luminous, although extremely hot flame; and in this process the hydrogen combines with the oxygen of the air, forming water. The production of water by the combustion of hydrogen in the air may easily be shown by bringing a bright dry glass over the flame of hydrogen issuing from a fine jet, as in Fig. 7; the glass becomes at once dimmed owing to the condensation of water in small drops upon the cold dry surface. A number of these drops can be collected, and, upon examination, they are found to consist of pure water. Hydrogen does not support the combustion of a candle, nor the life of an animal. If a burning taper is pushed up into a cylinder of this gas, held with its mouth downwards, the hydrogen burns at the mouth of the jar, while the taper is extinguished; it can, however,

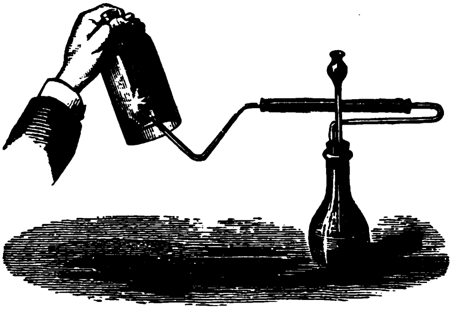

FIG. 7.

be relit by the flame at the mouth. Hydrogen can be poured from one vessel to another in the air; but as it is lighter than air it must be poured upwards. The specific gravity of hydrogen, when air is taken as the unit, is found to be 0·0693; but for several reasons we shall find it more convenient to take hydrogen itself as our unit, and compare the weight of the same volumes of other gases with hydrogen instead of air. One liter of hydrogen gas at 0° C. and 760 mm. pressure weighs 0·0896 grams. It is absorbed in considerable quantities by the metals palladium and platinum the product retaining its metallic appearance (see p. 174) Hydrogen, like oxygen, and all the other gases can be liquefied by the application of great cold and great pressure. This was proved independently by Cailletet in France and by Pictet in Geneva. The temperature needed to liquefy hydrogen is probably below −200°.

[The pupil must carefully work out the examples and exercises given for each Lesson at the end of the book, and thus test the accuracy of his knowledge.]

LESSON III.

PHYSICAL PROPERTIES OF GASES, ETC.

IT becomes now of importance to ascertain not merely the *weights* of oxygen or hydrogen capable of being evolved by using given weights of potassium chlorate or zinc, but likewise the *volume* of each gas thus obtained. Before we can enter into these calculations there are several important preliminary subjects, with the principles of which we must make ourselves acquainted.

The first of these is the *metric* or French decimal system of weights and measures; the second is the mode of measuring temperature, and the construction and use of thermometers, together with the laws regulating the expansion of gases by heat; whilst the third relates to the measurement of atmospheric pressure by means of the barometer, and the laws regulating the changes which variations of pressure produce in the volumes of gases.

Metric System of Weights and Measures.

There are several distinct advantages to be gained by the adoption of this system, the chief of which is that the system is throughout a decimal one, and hence all calculations for reduction, such as occur in our old measures (from pennyweights to tons, or from inches to miles, for instance), are avoided. A second important consideration which renders our use of this system advisable, is that it is now generally adopted by men of science in all countries. The starting point of this system is the establishment of a unit of length called a *meter*, equal to rather more than one yard (more exactly, 39·37 English inches). This meter, like all other standards of length, is an arbitrary length: a standard meter was prepared, and of this, copies are made for use.[1]

The meter is divided into tenths, hundredths, and thousandths; these parts are termed respectively, *decimeters*, *centimeters*, and *millimeters*. The multiples of the meter, tens, hundreds, and thousands, are called *decameters*, *hectometers*, *kilometers*. The measures of area, or square measure, and those of capacity, or cubic measure, are easily obtained; we have square meters and square deci-, centi-, and milli-meters; we have also cubic meters and cubic deci-, centi-, and milli-meters; and we have the square and cubic measures derived from the multiples of the meter in the same way.

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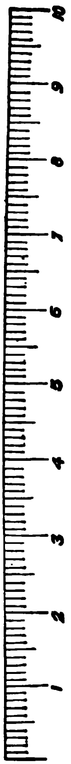
[1] When the meter was first made, it was intended to give it a length which should have some reference to the earth's circumference, and a standard was made which had the length of the $\frac{1}{10,000,000}$ part of the distance from the equator to the pole, as measured by the French geometricians. Subsequent investigations have, however, proved that the measurement of the earth's circumference then made is not quite correct, and hence the meter turns out to be not quite (although very nearly) the $\frac{1}{10,000,000}$ part of the true distance of the pole from the equator. The value of the metric system does not at all depend upon this relation between the earth's circumference and the meter. *The meter* is the length of the bar of metal carefully preserved in Paris, from which copies have been taken for use.

10 decimeters	1 meter.
100 centimeters	,,
1,000 millimeters	,,
100 square decimeters	1 square meter.
10,000 ,, centimeters	,,
1,000,000 ,, millimeters	,,
1,000 cubic decimeters	1 cubic meter.
1,000,000 ,, centimeters	,,
1,000,000,000 ,, millimeters	,,



The measure on the margin is 1 decimeter in length; it contains 10 centimeters and 100 millimeters. For the sake of simplicity the word *liter* is used to signify 1 cubic decimeter (rather less than an English quart).

The French philosophers who arranged this metric system wished to have a simple relation between the measure of volume and that of weight, and they determined to take as their unit of weight that of 1 cubic centimeter of pure water of the temperature of 4° Centigrade weighed at Paris. This weight is termed a *gramme*, or in English *gram*. It is divided like the meter into tenths, hundredths, and thousandths, called respectively deci-, centi-, and milli-gram; whilst to the tens, hundreds, and thousands of grams the names deca-, hecto-, and kilo-gram are given. A table showing the relation between the weights and measures of the metric system and those commonly in use in this country is given in the Appendix.

Measurement of Temperature.—Thermometers.

Measurements of changes of temperature are always effected by ascertaining the expansion or contraction which bodies undergo by alteration of temperature. For this purpose liquids are generally used, as solids expand too little, and gases too much, to be convenient indicators. Mercury and alcohol are the liquids commonly employed, especially the former, because its rate of expansion is nearly uniform, and because the range of temperature which can be measured by a mercurial thermometer is large, this metal boiling at a very high temperature and freezing at a comparatively low one. Alcohol is used when low temperatures have to be measured, as this liquid freezes with the greatest difficulty. Air thermometers are only used in very delicate experiments in physics. For temperatures above 350° instruments termed *pyrometers* are employed; these are, however, rarely required by the chemist.

In order to prepare a mercurial thermometer a straight piece of glass-tubing, having a bore as uniform as possible throughout its whole length, is taken, and a bulb blown upon the end. This bulb, together with the whole of the tube, is then filled with mercury, and heated up to the highest temperature which the instrument is required to measure; the open end of the tube is then completely closed, whilst full of mercury, by melting the glass before the blowpipe. The thermometer thus prepared requires graduating, in order that its indications may be compared with those of any other. This graduation is effected: 1. By plunging the bulb and stem into finely-powdered and melting ice, and marking on the stem the point where the mercury stands. 2. By immersing the bulb and stem in the steam given off from water boiling in a metallic vessel, and marking off the point where the mercury then stands. Care must be taken during this last experiment that the height of the barometer be observed; the reasons for this precaution will be explained further on. Having obtained these two fixed points, it is easy to adapt a scale to the thermometer. Three scales, each of which is capable of being expressed in terms of the others, are at present in use: 1. The *Centigrade* scale. 2. *Fahrenheit's* scale. 3. *Réaumur's* scale. In the Centigrade scale (which we shall adopt, it being the one almost universally employed in scientific works, and in general use on the Continent) the space between these two points—called respectively the *freezing* and *boiling* points—is divided into 100 equal parts, each of which is called a *degree*: the Zero of the scale is placed at the freezing point, so that the boiling point is 100° C. Divisions equal in size to these are continued above the boiling and below the freezing points, and those below the freezing-point are characterised by a minus sign, thus, – 1° C., – 2° C., &c. Fahrenheit divided the same space into 180 equal parts, each of which is called a degree Fahrenheit; he did not, however, commence his scale at the freezing-point, as he erroneously thought that he had obtained the greatest possible degree of cold by making a mixture of snow and salt; the temperature of this mixture he found to be 32 of his degrees below the freezing-point of water; he, therefore, called the freezing-point 32°. In Fahrenheit's scale, minus numbers are employed to denote degrees of temperature below the Zero of his scale; this scale is the one in common use in England, but is the most inconvenient one which we could adopt. Réaumur's scale (used in Russia and Sweden) resembles the Centigrade scale, except that the space between the freezing and boiling points is divided into 80 equal parts; so that water boils at 80° Réaumur. The connection between these three scales is seen at a glance by reference to Fig. 8. The relation between the degrees Fahrenheit, Centigrade, and Réaumur is expressed by the numbers 9, 5, 4. In converting from degrees Fahrenheit to Centigrade or Réaumur, we must remember first to subtract 32 and then reduce; whilst when passing from degrees Centigrade and Réaumur to Fahrenheit we must add 32 after the multiplication and division are completed.

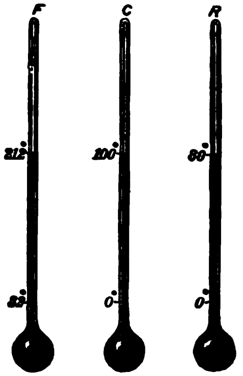


FIG. 8.

If very exact measurements are required, several precautions must be taken in the graduation and use of thermometers: thus, for instance, the tube must be calibrated —that is, the irregularities in the bore must be determined, and allowed for, whilst any slight alteration in the position of the freezing-point must from time to time be ascertained. Different mercurial thermometers often show slight differences in their indications, owing to the unequal expansion of different kinds of glass; hence it is necessary in exact experiments to have recourse to the air thermometer.

Expansion of Gases by Heat.

Solid and liquid bodies expand much less for equal increments of heat than gases; they also all expand differently, whilst all gases expand alike, or very nearly so. The expansion of solids and liquids is a subject with which, in elementary chemistry, we have little to do, whilst a knowledge of the laws regulating the expansion of gases is of more immediate importance. It has been found by exact and laborious experiment that all gases expand $\frac{1}{273}$ part of their volume at 0° C. for every increase in temperature of 1° Centigrade, and this is known as the Law of Charles.

Thus	273	volumes of air	or hydrogen	at 0° C.
become	274	,,	,,	1°
,,	275	,,	,,	2°
,,	276	,,	,,	3°
,,	273 + t	,,	,,	t°

The decimal fraction corresponding to $\frac{1}{273}$ is ·003665; 1 volume of air at 0° C. becomes 1·003665 volumes when heated to 1° C. This fraction is called the *co-efficient of the expansion of gases.*[1] If we require to know the volume which 1,000 cubic centimeters of hydrogen measured at 0° C. will occupy when the temperature is raised to 20°, we must remember that the alteration in bulk takes place in the ratio of the numbers 273 to 273 + 20. Hence we multiply 1,000 by 293, and divide by 273. If we require to know what the volume 1,000 cc. measured at 20° C. will occupy when the temperature sinks to 0°, we have to remember that the diminution in volume follows the same law, and that, therefore, 293 vols. at 20° will become 273 vols. at 0°. If we have 1,000 cc. of gas at 20°, and desire to know the volume which

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[1] Regnault and Magnus have shown that hydrogen gas expands rather less than atmospheric air, whilst carbonic acid gas expands rather more than air. The co-efficients of expansion from 0° to 100° obtained by these two renowned experimentalists are as follows:—

	Regnault.	*Magnus.*
Hydrogen	0·36614	0·36556
Carbonic Acid . . .	0·37099	0·36909

it will occupy at 50°, we have in like manner to remember, that 273 + 20, or 293 vols. at 20° become 273 + 50, or 323 vols. at 50° ; and then we can easily find the alteration in volume which the 1,000 cc. of gas will undergo when heated from 20° to 50°.

Relation of Volume of Gases to Pressure.

When a gas is subjected to an increase of pressure, the volume of the gas becomes less ; and when the pressure is withdrawn, the gas immediately expands again, and occupies exactly the same volume which it did before the pressure was increased. Solid and liquid bodies cannot be compressed in the same way. Gases are hence known as *compressible fluids*, and liquids as *incompressible fluids :* liquids, however, really are compressible, but only to a very slight extent ; like gases, they recover their original volume on removal of the pressure. The law representing the relation between the volumes of a gas and the pressures to which the gas is subjected is a very simple one : it is termed *Boyle's* or *Mariotte's Law*, from the names of the discoverers : it states that the *volume occupied by any gas is inversely proportional to the pressure to which it is subjected.* Thus, for instance, the volume 1 under pressure 1 becomes the volume 2 under the pressure ½, the volume 3 under the pressure ⅓, the volume ½ under the pressure 2, and the volume ⅓ under the pressure 3, and so on.[1] For a description of the experimental proof of this law, a work on Physics must be consulted.

The instrument which serves to measure the pressure exerted by the air is termed a *barometer* (Fig. 9). This in its simplest form consists of a straight glass tube, about 800 mm. (32 inches) in length, closed at one end, and furnished with a millimeter scale. This tube is filled with dry mercury, and the open end placed downwards in a basin containing the same metal. It is then seen that the mercury sinks in the tube to a point about 760 mm. from the surface of the metal in the basin : it is sustained in this position by the pressure of the air. When this pressure increases, the height of the sustained column becomes greater; when it diminishes, the level of the mercury in the tube falls. All gases generated at the earth's surface are subject to this pressure, and their volumes increase or diminish according to the above law, as the superincumbent pressure becomes less or greater.

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[1] This law, like many other physical laws, is only an approximation to the truth as ascertained by exact experiment. No gases obey the law exactly when high pressures are used, as all gases can be liquefied by great pressure and great cold, and many deviate perceptibly long before the point of liquefaction is reached ; still, as these deviations are but very slight, we may assume, for the purposes of our calculations, and when the changes of pressure are not very large, the absolute truth of the law of Boyle.

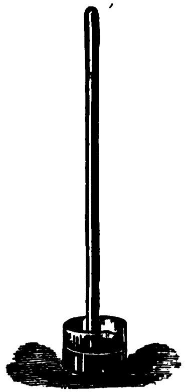

FIG. 9.

In estimating the volume of hydrogen which can be collected from a given weight of zinc and sulphuric acid, it is clear that we require to know not only the temperature at which the gas is collected, but also the atmospheric pressure under which it is measured ; and in order to be able to compare the bulks of two gases, we must always compare them under like conditions of temperature and pressure. For this purpose we agree to compare all the volumes of gases at the *standard temperature of* 0° C. and under the *standard pressure of* 760 *millimeters of mercury*. Suppose now that we desire to know what weight of potassium chlorate we need to take in order to fill with oxygen gas a gasholder having a capacity of 10 liters, the temperature of the room being 15° C. and the barometer standing at 752 mm. We know (1) that 122·29 parts by weight of potassium chlorate yield 47·88 of oxygen ; (2) that a liter of oxygen at 0° C. and 760 mm. weighs 1·4298 grams. We must now ask: What volume will 10 liters of oxygen occupy if measured at 0° C. and under the pressure of 760 mm.? The volume will be $\frac{10 \times 752 \times 273}{760 \times (273+15)} = 9{\cdot}38$ liters. But 1 liter of oxygen measured at 0° and 760 mm. weighs 1·4298 grm., 9·38 liters measured under the same circumstances will weigh 13·413 grms. Next we require to know how many grams of potassium chlorate will furnish this weight of oxygen ; as every 122·29 parts of chlorate yield 47·88 parts of oxygen we shall need $\frac{122{\cdot}29 \times 13{\cdot}413}{47{\cdot}88} = 34{\cdot}26$ grams of potassium chlorate. In the same way we can calculate, for instance, the weight of zinc and sulphuric acid needed to inflate a balloon of the capacity of 150 cubic meters with hydrogen when the thermometer stands at 11° C. and the barometer at 763 mm.

[The student will do well to work out numerous examples of this kind, in order to familiarize himself with these methods of calculation (see Exercises at the end of the book, and also, Thorpe's *Questions in Chemistry*).]

Diffusion of Gases.

Another physical property of gases is that of *diffusion*. Gases which, when brought into contact with one another, do not combine chemically, have the power of becoming intimately mixed together, even when differing in specific gravity, and when the heavier gas is placed at the bottom, and both remain at rest. This important property is called the *diffusive power of gases*. The rate at which gases diffuse varies greatly. Thus, a bottle filled with hydrogen lost 94·5 per cent. of this gas when left exposed to the air in the same time as that in which a bottle of carbonic acid lost only 47 per cent. of this gas in the same way. Gaseous diffusion goes on through the minute pores of certain solids, such as stucco, or thin plates of graphite ; the different diffusive rates of air and hydrogen may be well seen by fixing a thin piece of stucco on to one end of a glass tube open at the other end, and filling this with hydrogen ; on plunging the open end into water a steady rise of this liquid in the tube is noticed, and after some time the whole of the hydrogen is found to have disappeared, and the tube contains only pure air. Experiments made upon this subject have shown that the *velocity of diffusion of different gases is inversely proportional to the square roots of their densities ;* thus 4 volumes of hydrogen will pass through the diaphragm in the same time that 1 volume of oxygen is able to do so, oxygen being sixteen times as heavy as hydrogen. This property of gases has an important bearing upon the atmosphere of towns and dwelling-rooms, which is kept pure to a great extent by this diffusive power of gases.

The following table gives the rates of diffusion, as determined by Graham, of several gases, that of air taken to be equal to 1, compared with the inverse square roots of their densities, air also taken as the unit :—

	Density air = 1.	$\frac{1}{\sqrt{\text{density}}}$	Velocity of diffusion air = 1.
Hydrogen	0·06926	3·7790	3·830
Nitrogen	0·97130	1·0150	1·014
Oxygen	1·10560	0·9510	0·949
Carbon dioxide.	1·52900	0·8087	0·812

LESSON IV.

OXIDES OF HYDROGEN.

WE are acquainted with two compounds of oxygen and hydrogen, namely :—

(1) *Water* or *Hydrogen Mon-oxide.* Symbol H_2O. Molecular Weight 17·96, Density 8·98.

(2) *Hdyrogen Di-oxide.* Symbol H_2O_2. Molecular Weight 33·92.

Water.

When hydrogen burns in the air water is formed by the union of the former gas with oxygen. The discovery of the composition of water was made in 1781 by Henry Cavendish, who showed that two volumes of hydrogen unite with one volume of oxygen to form water. In order to prove this, Cavendish made a mixture of these gases in this proportion by volume in a jar, and then allowed them to pass into a strong dry glass vessel shown in Fig. 10, A, from which the air had been pumped out. By means of two platinum wires melted through the glass (at B), an electric spark could be passed through the mixture of two gases, causing their explosive combination: dew was then seen to be deposited upon the sides of the vessel, and when the stopcock was opened under water, this liquid rushed in, filling the whole space formerly occupied by the mixed gases. Cavendish weighed the vessel before and after the explosion, and, knowing the weight of the gases taken, he found that the weight of the water produced was the same as that of the gases which combined.

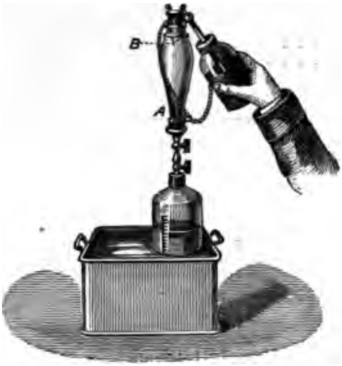

FIG. 10.

Composition of Water by Volume.

Since the above-mentioned year, the exact composition of water has been made the subject of careful synthetical experiment by many chemists, and the result has been to confirm by much more delicate methods this original conclusion. The most accurate of these methods of ascertaining the composition of water is a modification only of that originally used by Cavendish. We employ for this purpose a long, accurately graduated, strong glass tube called a *Eudiometer* (A, Fig. 11), open at one end and closed at the other, whilst through the glass at the top are melted two platinum wires. This tube is first filled with mercury, and placed mouth downwards over a trough filled with this metal Hydrogen gas is now allowed to enter the tube, and the volume admitted measured (suppose it equal to 100 volumes); oxygen gas is next admitted, and the volume of the two mixed gases measured (suppose that 75 volumes of oxygen are added). In making this experiment, care must, however, be taken that the temperature and atmospheric pressure are carefully measured by means of the thermometer (*t*) and the barometer (B) shown in the figure; it is also necessary that the tube be not more than half full of the gaseous mixture, as great heat is evolved by the combustion, and hence a sudden increase of volume occurs, for which reason it is necessary to press down the open end of the tube upon a plate of caoutchouc placed under the mercury. An electric spark is now passed through the gas along the platinum wires, when a flame is seen to pass down through the gas, showing that combination has occurred; the water produced will be deposited as dew upon the inside of the tube, and will then only take up about $\frac{1}{2000}$ part of the bulk which its constituent gases occupied, so that its volume may be neglected. When the bottom of the eudiometer is opened, the column of mercury in the tube rises, and we shall then find that only 25 volumes of gas remain, and this turns out

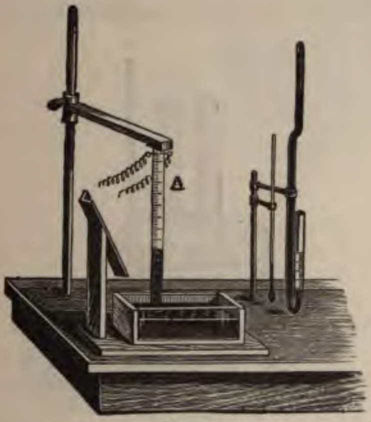

FIG. 11.

to be pure oxygen. Thus we see that 100 volumes of hydrogen require exactly 50 volumes of oxygen for their complete combustion. By a modification of this experiment, it can be shown that the volume of the gaseous water formed occupies exactly 100 volumes; or 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam, hence the density of steam or weight of 1 volume is $\frac{15{\cdot}96 + 2}{2} = 8{\cdot}98$.

The most striking method of demonstrating the composition of water analytically is by splitting it up into its constituent gases by means of a current of voltaic electricity. For this purpose we will fill a glass vessel (Fig. 12) with water acidulated with sulphuric acid to enable it to conduct the electricity, and bring two test-tubes filled with water and inverted into this vessel over two small platinum plates attached to wires of the same metal passing through the caoutchouc stopper at the bottom of the glass; on connecting these with the terminals of a battery of three or four of Grove's elements, an evolution of gas from each plate is noticed: that disengaged from the plate in connection with the platinum end of the battery is found to be pure oxygen; whilst that coming off from the other plate connected with the zinc end of the battery is pure hydrogen gas. If the two tubes be graduated,

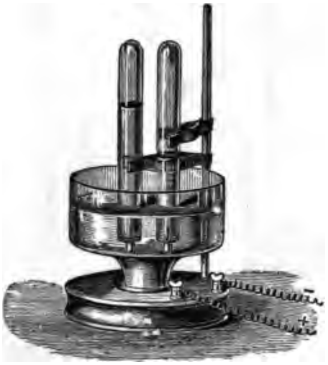

FIG. 12.

it will be seen that the volume of the hydrogen is a very little more than double that of the oxygen; for, owing to the fact that oxygen is rather more soluble in water than hydrogen, we do not in this way get quite the exact proportions. In order to collect the detonating mixed gases evolved by this *electrolytic decomposition* of water, an apparatus represented in Fig. 13 may be employed.

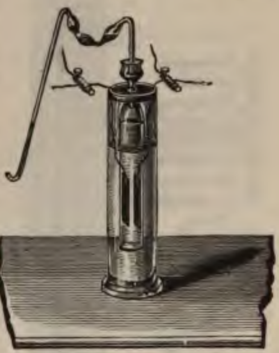

FIG. 13.

Composition of Water by Weight.

Oxygen being 15·96 times as heavy as hydrogen, and these gases combining to form water in the proportions by volume of one volume of the former to two of the latter, we now know that the proportions by weight in which these gases exist in water must be as 15·96 to 2. It is nevertheless most important that this calculation be verified by direct experiment. For this purpose, use is made of the fact that copper oxide when heated alone does not part with any of its oxygen, but when heated in presence of hydrogen it parts with as much oxygen as will, by combining with the hydrogen, form water, being itself wholly or partly reduced to metallic copper. If, therefore, we take a known weight of copper oxide, heat it, and pass pure hydrogen over it until it has parted with all its oxygen, and if we collect and weigh all the water thus formed, and likewise weigh the remaining metallic copper, we shall have made a *synthesis by weight of water*. For the loss in weight of the copper oxide is the weight of oxygen which has combined with hydrogen to form water; and the difference between this weight and that of the water formed, is the weight of the hydrogen thus combined. The arrangement used for this determination is represented in Fig. 14. The hydrogen evolved by zinc from sulphuric acid in the bottle on the left hand is purified from any trace of arsenic, sulphur, and moisture which it may contain by passing through the U-tubes, numbered 1 to 7, Fig. 14, containing absorbent substances. The tube No. 8, containing a very hygroscopic substance, is weighed both before and after the experiment: and if no increase occurs, the dryness of the gas is insured. The gas then comes in a perfectly pure state into contact with the heated copper oxide contained in the bulb A. This first bulb, which is accurately weighed, is placed in connection with a second bulb B, in which the water formed by the reduction of the oxide collects; any moisture which may escape condensation in this bulb is retained in weighed drying tubes, 9 to 12, containing fragments of pumice moistened with sulphuric acid. Most careful experiments made according to this method, carried out with many precautions which cannot here be detailed, have shown that 88·86 parts of oxygen by weight unite with 11·14 parts of hydrogen to form 100 parts of water.

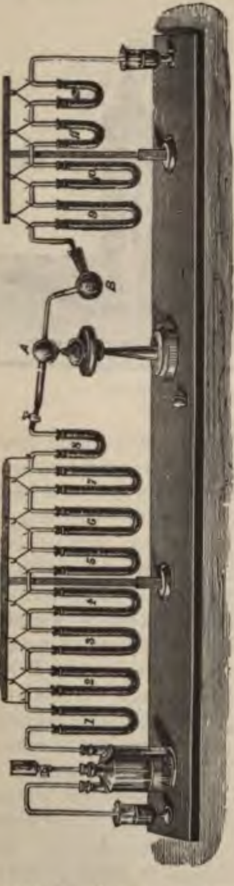

Fig. 14

Free oxygen and hydrogen combine together, when a light is brought in contact with them, with so much force that a violent and dangerous explosion occurs from the sudden expansion caused by the great heat evolved in combination. If we fill a strong soda-water bottle one-third full of oxygen and two-thirds of hydrogen, and then bring a flame to the mouth, the gases combine, producing a sudden detonation like the report of a pistol. Many fatal accidents have occurred to persons who have carelessly experimented with large volumes of this explosive mixture. In order to exhibit the great heat evolved by the combination of the two gases, the *oxyhydrogen blowpipe* is employed; in this arrangement the gases are contained separately in two caoutchouc bags, being only brought together at the point at which the combination is desired to take place, so that all danger of explosion is avoided. The flame thus produced is very slightly luminous, but its temperature is so high, that the most difficultly fusible metals, such as platinum, may be easily melted in it, whilst iron wire held in the flame burns with beautiful scintillations, forming an oxide of iron. A piece of chalk or lime placed in this flame becomes heated to bright whiteness, and emits an intense light, known as the *oxyhydrogen lime-light*, largely employed for signal purposes, lanterns, &c.

Properties of Water.

Water exists in nature in three forms: in the solid form as ice, in the liquid state as water, and in the gaseous form as steam. At all temperatures between 0° and 100° C. it exists in the liquid state, and above 100° it entirely assumes the gaseous form (under the ordinary atmospheric pressure of 760 mm.). The melting-point of ice is always found to be a constant temperature, and hence it is taken as the zero of the Centigrade scale; water may, however, under certain conditions, be cooled below 0° C. without becoming solid; but ice can never exist at a temperature above 0° C. In passing from the solid to the liquid state, water becomes reduced in volume, and on freezing a sudden expansion (from 1 volume to 1·09) takes place. That this expansion exerts an almost irresistible force is well illustrated by the splitting of rocks during the winter. Water penetrates into the cracks and crevices of the rocks, and on freezing widens these openings; this process being repeated over and over again, the rock is ultimately split into fragments. Hollow balls of thick cast-iron can thus easily be split in two by filling them with water and closing by a tightly fitting screw; and then exposing them to a temperature below 0° C.

In the passage from solid ice to liquid water, we not only *elastic force*, or *tension* of aqueous vapour; it may be measured, when a small quantity of water is placed above the mercury in a barometer, by the depression which the tension of the vapour thus given off is capable of exerting upon the mercurial column (as in Fig. 9). If we gradually heat the drops of water thus placed in the barometer, we shall notice that the column of mercury gradually sinks; and when the water is heated to the boiling-point, the mercury in the barometer tube is found to stand at the same level as that in the trough, showing that the elastic force of the vapour at that temperature is equal to the atmospheric pressure. Hence *water boils when the tension of its vapour is equal to the superincumbent atmospheric pressure.* On the tops of mountains, where the atmospheric pressure is less than at the sea's level, water boils at a temperature below 100°: thus at Quito, where the mean height of the barometer is 527 mm., the boiling-point of water is 90°·1; that is, the tension of aqueous vapour at 90°·1 is equal to the pressure exerted by a column of mercury 527 mm. high. Founded on this principle, an instrument has been constructed for determining heights by noticing the temperatures at which water boils. A simple experiment to illustrate this fact consists in boiling water in a globular flask, into the neck of which a stopcock is fitted: as soon as the air is expelled, the stopcock is closed, and the flask removed from the source of heat; the boiling then ceases; but on immersing the flask in cold water the ebullition recommences briskly, owing to the reduction of the pressure consequent upon the condensation of the steam; the tension of the vapour at the temperature of the water in the flask being greater than the diminished pressure. All other liquids obey a similar law respecting ebullition; but as the tensions of their vapours are very different, their boiling-points vary considerably.

When steam is heated alone, it expands according to the law previously given for permanent gases; but when water is present, and the experiment is performed in a closed vessel, the elastic force of the steam increases in a far more rapid ratio than the increase of temperature. The following table gives the tension of aqueous vapour, as determined by experiment, at different temperatures measured on the air thermometer.

Tension of the Vapour of Water.

Temperature, Centigrade.	Tension in millimeters of mercury.	Temperature, Centigrade.	Tension in atmospheres, 1 atmosphere = 760 mm. of mercury.
− 20°	0·927	100°	1
− 10	2·093	111·7	1·5
0	4·600	120·6	2
+5	6·534	127·8	2·5
10	9·165	133·9	3
15	12·699	144·0	4
20	17·391	159·2	6
30	31·548	170·8	8
40	54·906	180·3	10
50	91·982	188·4	12
60	148·791	195·5	14
70	233·093	201·9	16
80	354·280	207·7	18
90	525·450	213·0	20
100	760·000	224·7	25

We now see why the barometric height must be noticed in graduating a thermometer (page 25); if the height differ from 760 mm. the temperature of the water boiling under that pressure will not be quite 100° C. A metal vessel is here employed, because it is found that water does not always boil at 100° in glass vessels, even though the atmospheric pressure be 760 mm., owing to some molecular action analogous to cohesion between the glass and water.

Pure water and ice, when seen in large masses, are found to possess a blue colour; this is clearly noticed in the glaciers and lakes of Switzerland.

In order to obtain pure water the chemist is obliged to *distil* river or spring water (that is, to boil the water and collect the water formed by the condensation of the steam thus produced), as all naturally occurring water contains more or less *solid matter in solution* derived from the surface of the earth over which the water flows ; this dissolved solid matter is left behind on boiling off the water. *Solid matter in suspension* can be got rid of by the simpler process of *filtration* through paper, sand, &c. An arrangement for distillation on a small scale, as used in laboratories, is seen in Fig. 16 ; it consists of a glass retort in which the impure water is placed, connected with a condenser, made of two glass tubes, between which a current of cold water is made to circulate. The distilled water is collected in the flask placed at the end of the apparatus.

Rain-water is the purest form of water occurring in nature, but even this contains impurities derived from the dust, &c., in the air, and no sooner does it touch the earth's surface than it dissolves some of the materials with which it comes in contact, and, according to the nature of the ground over which it passes, becomes more or less impure. All fresh-water on the earth's surface has been derived from the ocean by a vast process of distillation, having been deposited in the form of rain or snow from the atmosphere.

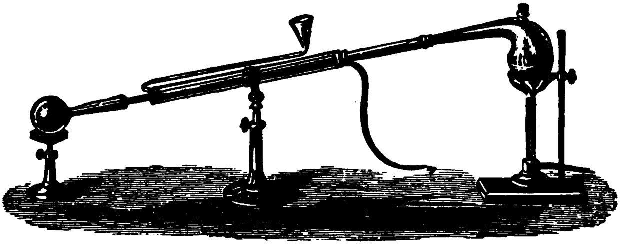

FIG. 16.

All the rain-water ultimately passes in the form of spring-water, or river-water, into the sea, carrying with it the soluble constituents which have been dissolved out from the strata through which it has percolated. In consequence of this continual accession of soluble salts, and removal of pure water by evaporation, the sea-water is rendered salt ; it contains about 35 parts of solid matter (28 of which consist of common salt, or sodium chloride) in solution in 1,000 parts of water.

Water is the most general solvent for chemical substances with which we are acquainted. Most salts are soluble to a greater or less extent in water, and are deposited again in crystals when the water is evaporated ; we are unacquainted with any simple general law regulating the quantities of salts taken up by water ; in most cases the solubility is greater in hot than in cold water, and in all cases a given volume of water at a definite temperature is capable of dissolving as a maximum a fixed quantity of salt—this maximum differing for every salt. Such a solution is said to be a saturated solution. Water is also contained in the solid state in combination as *water of crystallization* in many salts ; when this water is driven off by heat, the crystal falls to powder. Gases also dissolve in water in quantities varying with the nature of the gas, the temperature, and the pressure to which the gas is subjected. It is solely in consequence of the presence of oxygen derived from the air dissolved in the water of lakes, rivers, and seas, that fish are enabled to keep up their respiration ; as the water passes through their gills the oxygen is taken up to purify their blood.

Hydrogen Di-oxide.

Symbol H_2O_2.—This substance has received the name of oxygenated water, as it easily decomposes into oxygen and water : it is found to contain twice as much oxygen as water does, consisting of 2 parts by weight of hydrogen combined with 31·92 of oxygen ; hence, if we represent water by the symbol H_2O, hydrogen di-oxide will be written H_2O_2. It does not occur in nature, but is artificially prepared by acting on barium di-oxide, BaO_2, with dilute sulphuric acid, H_2SO_4: an exchange takes place between the barium and hydrogen, giving rise to hydrogen di-oxide and barium sulphate. Thus

$$\begin{array}{l|l} Ba & O_2 \\ SO_4 & H_2. \end{array}$$

Hydrogen di-oxide may also be prepared by passing carbonic acid gas through barium di-oxide suspended in water, when barium carbonate separates out as a white powder insoluble in water, and hydrogen di-oxide remains in solution. The reaction is represented by the following equation :—

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

The aqueous solution of the di-oxide is concentrated by being allowed to evaporate under the receiver of an air-pump, when it attains a specific gravity of 1·452 and consists of the pure di-oxide. Hydrogen di-oxide is chiefly characterised by the ease with which it loses half its oxygen; this gas is slowly given off at 20°, but at 100° C. the evolution of oxygen becomes very rapid. In consequence of the readiness with which it gives off oxygen, hydrogen di-oxide acts as a powerful bleaching agent, rapidly oxidizing and destroying vegetable colouring matter. Hydrogen di-oxide liberates iodine from a solution of potassium iodide, and this takes place in presence of ferrous sulphate, a reaction which distinguishes this compound from all other oxidizing agents. A remarkable decomposition occurs when this substance is brought in contact with ozone, common oxygen and water being produced. Another interesting reaction occurs when silver oxide is brought together with hydrogen di-oxide, the silver oxide being reduced to metallic silver, whilst water and free oxygen are formed. The explanation of this peculiar reaction will be given further on (see p. 160).

LESSON V.

NITROGEN.

Symbol N, *Atomic Weight* 14·01, *Density* 14·01.—Nitrogen exists in the free state in the air, of which it constitutes four-fifths by bulk; it occurs combined in the bodies of plants and animals, and in various chemical compounds, such as *nitre*, whence the gas derives its name (generator of nitre). It is best obtained from the air by taking away the oxygen with which it is mixed; for this purpose we may burn a piece of phosphorus in a bell-jar filled with air, the mouth of which is placed in a vessel full of water. White fumes of a compound of phosphorus and oxygen, called phosphorus pentoxide, at first fill the jar, but these soon subside and dissolve in the water, leaving the nitrogen in a nearly pure state. One-fifth of the original volume of the air, consisting of oxygen, will have disappeared. Nitrogen may also be prepared by passing air over red-hot metallic copper, which combines with the oxygen, forming solid copper oxide, and leaves the gaseous nitrogen in a pure state. Nitrogen is also formed when a current of chlorine is passed through an excess of a solution of ammonia; nitrogen gas is evolved, and sal-ammoniac remains behind in solution. If the chlorine be present in excess, a most dangerous and explosive compound is formed (p. 108).

Nitrogen is also formed by the decomposition of some of its compounds; thus, ammonium nitrite when heated yields nitrogen and water.

$$NH_4NO_2 = N_2 + 2H_2O.$$

Nitrogen is a colourless, tasteless, inodorous gas, slightly lighter than air (specific gravity 0·972, air being 1·0). At a very low temperature and under a high pressure nitrogen condenses to a colourless liquid, its boiling point being about—193°. Nitrogen when cooled to a still lower temperature has been solidified to a snow-like crystalline mass. Nitrogen gas does not combine readily with bodies, it is a very inert substance, neither supporting combustion nor animal life, nor burning itself: it has, however, no poisonous properties, and animals plunged into a jar of this gas die simply of suffocation from the want of oxygen. Nitrogen can be made to unite with both oxygen and hydrogen; when combined with the latter it forms a powerful alkaline base, *ammonia*, and united with both elements, it forms a strong acid, *nitric acid.*

The Atmosphere.

The Atmosphere is the gaseous envelope encircling the earth; and it constitutes the ocean of air at the bottom of which we live. We become aware of the existence of the air when we move rapidly, and experience the resistance offered to the passage of our bodies, and also when the air is in motion, giving rise to a wind. We notice the pressure of the atmosphere if we withdraw the air from beneath the hand by a powerful air-pump, for we then find that the hand is pressed down with a force equal to 1·033 kilos. on a square centimeter, or nearly 15 lbs. on every square inch. The total atmospheric pressure which the human body has to support hence amounts to several tons, but this pressure is not felt under ordinary circumstances because the pressure is exerted equally in every direction. The instrument used for measuring the pressure of the air is termed a Barometer (see Fig. 9, p. 29), and the average pressure at the sea-level is equal to that exerted by a column of mercury 760 mm. high. The air being elastic and having weight, it is clear that the lower layers of air must be more compressed than those above them, and hence the density of the air must vary at different heights above the sea-level. The density of the air being thus dependent on the pressure to which it is subjected, the higher strata of air become extremely rarefied, and it is hence difficult to say exactly whereabouts the air ceases; but it appears that the limit of the atmosphere is about 45 miles from the level of the sea. If the whole atmosphere were of the same density throughout as it is at the earth's surface, it would only reach to a height of a little more than 5 miles above the sea-level. The weight of one liter of dry air at 0° and under 760 mm. of pressure is 1·2932 grams. Atmospheric air has been liquefied by Pictet and Cailletet, and also by Wroblewski, who has ascertained that its boiling point is – 192°, and has shown that the oxygen and nitrogen do not separate from each other when air is liquefied.

Respecting the *chemical composition of the atmosphere* we have to remark, in the first place, that the air is a mixture, and not a chemical compound of its constituent gases, although, as we shall see, these occur throughout the atmosphere in almost unvarying proportions. The grounds for coming to this conclusion are, first, that if we bring oxygen and nitrogen together in the proportions in which they are found in air, no elevation of temperature or alteration in bulk occurs (as is invariably the case when gases combine), and yet the mixture acts in every way like air; secondly, that the relative quantities of the two gases present are not those of their combining weights, nor of any simple multiples of these weights; and thirdly, that although in general the proportions of the two gases are constant, yet instances not unfrequently occur in which this ratio is different from the ordinary one. The most convincing proof, however, that air is not a chemical compound is derived from an experiment upon the solubility of air in water: when air is shaken up with a small quantity of water, some of the air is dissolved by the water; this dissolved air is easily expelled again from the water by boiling, and on analysis the expelled air is found to consist of oxygen and nitrogen in the relative proportions of 1 and 1·87. Had the air been a chemical compound, it would be impossible to decompose it by simply shaking it up with water; the compound would then have dissolved as a whole, and, on examination of the air expelled by boiling, it would have been found to consist of oxygen and nitrogen in the same proportions as in the original air, viz. as 1 to 4. This experiment shows, therefore, that the air is only a mixture, a larger proportion of oxygen being dissolved than corresponds to that contained in the atmosphere, owing to this gas being more soluble in water than nitrogen.

There are many ways of determining the amounts of oxygen and nitrogen contained in the air, the best of these being by the *eudiometer*,[1] by means of which the composition by volume is ascertained. For this purpose the same arrangement is employed as that used in the eudiometric synthesis of water (Fig. 11). A quantity of air sufficient to fill the tube about one-sixth full is introduced into the eudiometer previously filled with mercury; the volume of this air is then accurately ascertained by reading off with a telescope the number of the millimeter divisions on the tube to which the mercury reaches, whilst the height of the column of mercury in the tube above the trough, together with that of the barometer and the temperature of the air, are also read off. A quantity of pure hydrogen gas more than sufficient to combine with all the oxygen present is now added; and the volume of this gas, and the pressure exerted upon it, determined as before. An electric spark is now passed through the mixture, care having been taken to prevent any escape of gas by pressing the open end of the eudiometer against a sheet of caoutchouc under the mercury in the trough. After the explosion the volume is again determined as before, and is found to be less than that before the explosion, the whole of the oxygen and part of the hydrogen having combined to form water; the diminution, therefore, represents exactly the volumes of these gases which have united. We know, however, from our previous experiments upon the composition of water, that 2 volumes of hydrogen always unite with exactly 1 volume of oxygen to form water: hence one-third of the diminution in volume must represent the oxygen which has disappeared, and therefore, the volume of oxygen contained in the air taken. An example may make this clearer. Suppose the volume of air taken amounted to 100 vols., and that after the addition of hydrogen the volume of the mixture was 150 vols.; after the explosion 87 vols. were found to remain, that is, 63 volumes had disappeared; then $\frac{63}{3} = 21$ will be the volume of oxygen contained in 100 volumes of air.

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[1] From *εὐδία*, clear weather, and *μετρόν*, a measure: a measure of the clearness or purity of the air; that is, of the quantity of oxygen which it contains.

Analyses of air collected in various parts of the globe thus made with the greatest care have shown that the relative quantities of oxygen and nitrogen remain the same, or very nearly the same, from whatever region the air may have been taken. So that whether the air be derived from the tropics or the arctic seas, from the bottom of the deepest mine or from an elevation of 20,000 feet above the earth's surface, it contains from 20·9 to 21 volumes of oxygen per cent.

Composition of Air by Weight.—When we know the composition of air by volume, and the relative densities of the two constituent gases (14·01 for nitrogen and 15·96 for oxygen), we can calculate its composition by weight; we thus find that in 100 grams of air 23·14 grams of oxygen are mixed with 76·86 grams of nitrogen. It is important to control this calculation by experiment; for this purpose a large glass globe (Fig. 17), furnished with a stopcock (*u*) is rendered vacuous by the air-pump and then weighed; a tube (*a b*) of hard glass filled with copper turnings and also furnished with stopcocks is likewise weighed. This tube is then heated to redness in a long tube-furnace, and connected at one end with the empty flask, at the other with a series of tubes (A, B, C,) filled with caustic potash and sulphuric acid, for the purpose of completely freeing the air passing through them from carbonic acid and aqueous vapour; the cocks are then slightly opened, and air allowed to pass slowly through the purifiers into the hot tube, where it is completely deprived of oxygen by the hot metallic copper, which is thereby oxidized, the nitrogen passing on alone into the empty flask. After the experiment is concluded, the cooled tube is again weighed, and the increase over the former weighing gives the quantity of oxygen, whilst the increase in weight of the globe gives the nitrogen. The mean of a large number of experiments thus made shows that 100 parts by weight of air contained 23 parts by weight of oxygen and 77 of nitrogen.

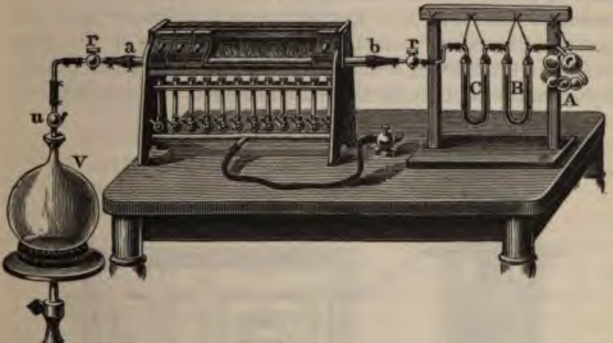


FIG. 17.

Carbonic Acid in the Air.—In addition to the two above-mentioned gases, the air contains several other important constituents, especially carbonic acid gas, aqueous vapour, and ammonia gas. We have already noticed (page 12) the important part which the carbonic acid gas of the air plays in the phenomena of vegetation, this gas being the source from which plants obtain the carbon they need to form their tissues. The quantity of carbonic acid present in the air is very small compared with the quantities of oxygen and nitrogen, being only from 3 to 4 volumes to 10,000 of air; nevertheless the absolute quantity of this gas contained in the whole atmosphere is enormously large (viz. about 3,000 billion kilos.). The quantity of carbonic acid contained in the air can be found by drawing a known volume of perfectly dry air (not less than 20 liters) through weighed tubes containing caustic potash; the increase in weight of the tubes gives the weight of carbonic acid contained in the air drawn through. Fig. 18 shows the arrangement of the apparatus; on the left is the aspirator, which, by means of the flow of a known volume of water from the upper to the lower vessel, causes the passage of an equal volume of air through the tubes; the two tubes farthest from the aspirator contain pumice-stone steeped in sulphuric acid,

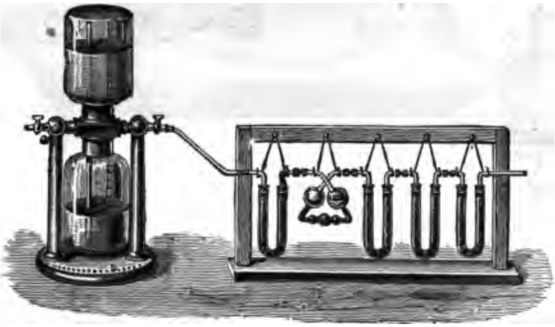


FIG. 18

and serve to dry the air completely before passing into the next tube and potash bulbs, in which the carbonic acid is absorbed by caustic potash: the tube nearest the aspirator also contains sulphuric acid and pumice to avoid a loss of moisture from the potash solution in the bulbs. The quantity of carbonic acid contained in the air in different localities and under different circumstances varies considerably—from 2 to more than 10 in 10,000 volumes of air. In houses and closed inhabited spaces, the quantity of carbonic acid present is often much larger, and the object of ventilation is to reduce the quantity of carbonic acid to as low a point as possible.

Other methods for the estimation of carbonic acid are described in the larger manuals.

Moisture in the Air.—Aqueous vapour is contained in the air in quantities varying in different localities and at different times, and depending mainly upon the temperature of the air. Air at a given temperature cannot contain more than a certain quantity of moisture in solution; and when it has absorbed this maximum quantity, it is said to be saturated with aqueous vapour. The higher the temperature of the air, the more water can it retain as vapour; and when air saturated with moisture is cooled, the water is deposited in the liquid form in very small globules, forming a mist, fog, or cloud. This is the cause of the fall of rain, snow, and hail. When warm air heavily laden with moisture from the ocean passes into a higher and colder position, or meets with a current of air of lower temperature, it cannot any longer retain so much aqueous vapour, and a large quantity assumes the liquid form, falling as rain when the temperature is above the freezing-point, or crystallizing as snow-flakes if the temperature be below that point. Hail is caused by the congelation of raindrops in passing through a stratum of air below the freezing-point. The quantity of rain thus deposited is very large: 1 cubic meter of air saturated with moisture at 25° C. contains 22·5 grams of water, and if the temperature of this air be reduced to 0° C. it will then be capable of retaining only 5·4 grams of water vapour; hence 17·1 grams of water will be deposited as rain. The air in England is often saturated with moisture, whilst the driest air observed on the coast of the Red Sea during a simoon contained only one-fifteenth of the saturating quantity. Instruments for ascertaining the degree of moisture or humidity of the air are termed *hygrometers.*

The deposition of dew is caused by the rapid cooling of the earth's surface by radiation after sunset, and by the consequent cooling of the air near the ground below the temperature at which it begins to deposit moisture.

The amount of aqueous vapour contained in the air at any time can be determined by the apparatus used for the estimation of the carbonic acid, for the moisture must be removed from the air before the carbonic acid can be absorbed, and the increase in weight of the tubes filled with pumice-stone moistened with sulphuric acid gives the weight of aqueous vapour. In general the air contains from 50 to 70 per cent. of the quantity necessary to saturate it. If the quantity be not within these limits, the air is either unpleasantly dry or moist.

Ammonia in the Air.—The next important constituent of the air is ammonia, which is a compound of nitrogen and hydrogen, and only exists in comparatively very minute quantities (about 1 part in 1,000,000 of air). Nevertheless it plays a very important part, as it forms one of the chief sources from which plants obtain the nitrogen they need to form their seeds and fruit. It has, however, been recently shown that certain leguminous plants have also the property of directly assimilating the nitrogen of the atmosphere.

Organic Matter in the Air.—Other substances which occur in the atmosphere in very small quantities may be considered as accidental impurities. Amongst them, volatile organic matter and floating organised germs are the most important, as probably influencing to a great extent the healthiness of the special situation. We become aware of the existence of the presence of organic putrescent substances when entering a crowded room from the fresh air; and it is probable that the well-known unhealthiness of marshy and other districts is owing to the presence of some organic impurity. Our knowledge of the floating organisms has of late years been greatly extended, and it is most probable that they are the cause of the various epidemic diseases.

Ozone is also present in fresh air, but absent in the close air of towns and dwelling-rooms, owing to its decomposition by the organic matter, &c., in such air; we do not know how it is formed in nature, unless it be by the discharge of atmospheric electricity.

LESSON VI.

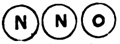
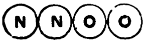
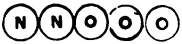
COMPOUNDS OF NITROGEN WITH OXYGEN.

We are acquainted with five distinct chemical compounds of nitrogen with oxygen, viz.

1	*Nitrogen Mon-oxide,*	containing	28	parts by weight of N.	to	16	of O.[1]
2	*Nitrogen Di-oxide*	,,	28	,,	,,	32	,,
3	*Nitrogen Tri-oxide*	,,	28	,,	,,	48	,,
4	*Nitrogen Tetr-oxide*	,,	28	,,	,,	64	,,
5	*Nitrogen Pent-oxide*	,,	28	,,	,,	80	,,

It will be seen that the oxygen contained in these compounds is in the proportion of the numbers 1, 2, 3, 4, 5, to one and the same quantity of nitrogen ; and here, for the first time, we meet with a striking example of the *law of chemical combination in multiple proportion.* Thus, while 28 parts by weight of nitrogen combined with 16 parts oxygen form 44 parts of nitrogen mon-oxide, we find that any other compounds of these two elements contain, combined with 28 parts of nitrogen, some simple multiple of 16 parts by weight of oxygen (thus, either 2 × 16, 3 × 16, 4 × 16, or 5 × 16), and that no compounds exist containing any intermediate quantity of oxygen.

This *law of combination in multiple proportions,* which is found to be true in all the numerous cases in which two or more elements combine to form several compounds, was first enunciated by John Dalton, and is the expression of well-established experimental facts. Dalton endeavoured to explain these facts by his celebrated *Atomic Theory.* He asked himself, Why do the elements combine only in multiples of their several combining proportions? and he answered the question by the following supposition.

Dalton's Atomic Theory.—Matter is made up of small indivisible portions which are called *Atoms* (ἀ privative, and τέμνω, I cut). The atoms of the different elements do not possess the same weights, but the relation between their weights is represented by that of the combining weights of the elements, which we may now properly designate as the *atomic weights* of the elements. Thus, the atom of oxygen is taken to be 16 times as heavy as the atom of hydrogen, and the weights of the atoms of nitrogen and oxygen as 14 to 16. Dalton further assumed that chemical combination consists in the approximation of the individual atoms to one another; and, having made these assumptions, he was able to explain why compounds must contain their constituents in the combining proportions, or in multiples of them, and in no intermediate proportion. Let us take, for example, the compounds of nitrogen and oxygen; the lowest of these consists of one single atom of oxygen combined with 2 atoms of nitrogen, or with one double atom of nitrogen, as it contains 16 parts of oxygen to 28 of nitrogen; thus, ; and we therefore write its formula, N_2O, and call it nitrogen mon-oxide. The next compound that can be formed must be produced by the addition of another atom of oxygen to this; thus we get  = N_2O_2, or nitrogen di-oxide. The next must be formed by the attachment of another atom of oxygen, and thus we get  = N_2O_3, or nitrogen tri-oxide. The next possible compound is

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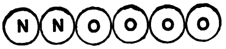
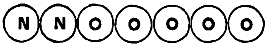
[1] For the sake of simplicity the whole numbers 14 and 16 are here taken instead of the exact numbers 14·01 and 15·96 as the combining weights of nitrogen and oxygen.

 = N_2O_4,

or nitrogen tetr-oxide: and the next

 = N_2O_5,

or nitrogen pent-oxide. We thus see that an atom being indivisible, no intermediate compounds can be formed. In considering this subject, we shall do well to remember that the Law of Combination in Multiple Proportions, being founded on experimental facts, stands as a fixed bulwark of the science, which must ever remain true; whereas the Atomic Theory, by which we now explain this great law, may possibly in time give place to one more perfectly suited to the explanation of new facts.[1]

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[1] If nitrogen di-oxide and nitrogen tetr-oxide be considered to be represented respectively by the formulæ N_2O_2 and N_2O_4, they will be exceptions to the law mentioned on page 58, respecting the density of compound gases or vapours, as instead of having their densities represented by the halves of their combining proportions, they will have them represented by the quarters of these numbers.

Adopting Dalton's views, chemists assume that the smallest particle of a chemical compound consists of a group of separate *atoms;* this group is called a *molecule;* it is supposed to be indivisible by mechanical forces, but can be separated into its constituent *atoms* by chemical means. Thus, the molecule of water consists of 2 atoms of hydrogen and 1 atom of oxygen, and the sum of the atomic weights of these constituents, 2 + 15·96 = 17·96, gives the *molecular weight* of water.

Combining Volumes of Gases.

It has been found that when gases unite together there is always a very simple relation between the volumes of the gases which enter into combination. Thus, for example, 2 volumes of hydrogen always unite with 1 volume of oxygen to form water; whilst 1 volume of hydrogen combines with 1 volume of chlorine gas (p. 98) to form hydrochloric acid. To explain this the hypothesis has been suggested that "*the densities of the elements known in the gaseous state are identical with their combining or atomic weights,*" and this conclusion has been borne out by subsequent results (Gay-Lussac). The subject will be considered more in detail in the chapter on "Atoms and Molecules" (p. 158).[1]

Hence it follows that the density and combining weight of oxygen, for example, are alike 15·96; or, oxygen is 15·96 times as heavy as hydrogen: the density and combining weight of nitrogen are alike 14·01; or, nitrogen is 14·01 times as heavy as hydrogen; the density of chlorine is 35·37, that of sulphur vapour 31·98, and so on. Remembering this fact it is easy to calculate the absolute weight of a given volume—say one liter of these different gases—when we know that one liter of hydrogen at the standard pressure and temperature weighs 0·0896 grams. Thus, under the same circumstances:—

1 liter of	oxygen	weighs	15·96 × 0·0896 = 1·430	grams.
,,	nitrogen	,,	14·01 × 0·0896 = 1·255	,,
,,	chlorine	,,	35·37 × 0·0896 = 3·169	,,
,,	sulphur vapour	,,	31·98 × 0·0896 = 2·865	,,

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[1] Certain exceptions to this law occur, of which the most important are those of phosphorus and arsenic, whose vapours possess a density twice as great as that required to be in accordance with the above law, and also of a few volatile metals, such as zinc and mercury, whose density is only half their atomic weight.

With respect to compounds, we find that *the density of a compound gas is one-half its molecular weight;* or the molecule of a compound gas occupies the space of 2 atoms of hydrogen.

Thus the density of water-vapour, or steam, H_2O, is $\frac{17{\cdot}96}{2} =$ 8·98, that is, it is about nine times heavier than hydrogen; the density of hydrochloric acid, HCl, is $\frac{36{\cdot}37}{2} = 18{\cdot}18$; that of ammonia, NH_3 is $\frac{17{\cdot}01}{2}$ or 8·5; that of carbonic acid, CO_2, is $\frac{43{\cdot}89}{2}$ or 21·94.

Hence the weights of 1 liter of these compounds (estimated at 0° C. and 760 mm.) are as follows :—

1 liter of steam	weighs	8·98 × 0·0896	grams.
,, ammonia	,,	8·5 × 0·0896	,,
,, hydrochloric acid	,,	18·18 × 0·0896	,,
,, carbonic acid	,,	21·94 × 0·0896	,,

Another method which may be used for calculating the relation between the weight and the volume of gases is the following :—

We have seen that one liter of hydrogen at 0° C. and 760 mm. pressure weighs 0·0896 grams, hence it is easy to calculate the volume occupied by 2 grams of hydrogen or its molecular weight, thus $\frac{2}{0{\cdot}0896} = 22{\cdot}32$ liters. Under similar conditions of temperature and pressure the molecules of all bodies in the gaseous state, whether simple or compound, occupy the same volume, and since hydrogen is taken as the standard of density for gases and vapours, it follows that the molecular weight (expressed in grams) of any element or compound will occupy 22·32 liters under normal conditions of temperature and pressure, thus:

22·32 liters of oxygen	weigh	2 × 15·96 = 31·92	grams.
,, ,, nitrogen	,,	2 × 14·01 = 28·02	,,
,, ,, chlorine	,,	2 × 35·37 = 70·74	,,
,, ,, sulphur vapour	,,	2 × 31·98 = 63·96	,,

and in like manner

22·32 liters of steam H_2O	weigh	2 + 15·96 = 17·96	grams.
,, ,, ammonia NH_3	,,	14·01 + 3 = 17·01	,,
,, ,, hydrochloric acid HCl	,,	1 + 35·37 = 36·37	,,
,, ,, carbon di-oxide CO_2	,,	11·97 + 31·91 = 43·89	,,

For ordinary calculations the approximate atomic weights 16, 14, 35·5, 32, &c., and the simpler number 22·3 liters, may be used.

The symbol for water, H_2O, therefore, not only indicates that it is composed of 2 parts by weight of hydrogen and 15·96 of oxygen, but also that 2 volumes of hydrogen have united with 1 volume of oxygen to form 2 volumes or one molecule of water-vapour. The symbol NH_3 denotes not only that 14 parts by weight of nitrogen combine with 3 parts by weight of hydrogen, but also that 3 volumes of hydrogen and 1 volume of nitrogen have united to form 2 volumes, one molecule, of ammonia, whilst the symbol HCl shows that 2 volumes of hydrochloric acid gas contain 1 volume of chlorine and 1 of hydrogen.

We have seen that 28 parts by weight of nitrogen unite with 32 parts of oxygen to form nitrogen di-oxide; the density of this compound is, however, found by experiment to be 15: hence its molecular weight is 30, consisting of 14 parts by weight of nitrogen to 16 of oxygen, or one volume of each constituent, and its molecular formula must, therefore, be NO.

Oxides, and Oxy-acids of Nitrogen.

Nitrogen and oxygen do not readily combine together, but under certain circumstances they are found to do so; thus, if a series of electric sparks are passed through a glass vessel filled with dry air, the presence of red-coloured vapours, possessing a peculiar acrid smell, is soon noticed. These consist of nitrogen tri- and tetr-oxides, formed by the union of the nitrogen and oxygen of the air. Fig. 19 illustrates the arrangements necessary for this purpose. A glass globe filled with air is furnished with two metallic wires, from the extremities of which the sparks from an induction coil can be passed through the air. After the rapid discharges have continued for a few minutes, portions of the oxygen and nitrogen have united to form a compound gas having a reddish brown colour, which may be easily recognised by holding a sheet of white paper behind the globe. These red fumes have the power (like ozone) of liberating iodine from iodide of potassium, hence the paper dipped in a solution of this salt and starch becomes at once blue when brought into the globe of air through which the sparks have passed.[1] If an alkali, such as potash, be present in the air through which the sparks are passed, a new substance called nitre, or potassium nitrate, is formed; and from this an important compound, called nitric acid, can be prepared. This substance is formed when flashes of lightning pass through the air, being carried down to the earth's surface in the rain. Nitric acid may be considered as a compound of nitrogen pentoxide with water; and, as all the other nitrogen oxides can be obtained from it, we shall first consider its properties and mode of preparation.

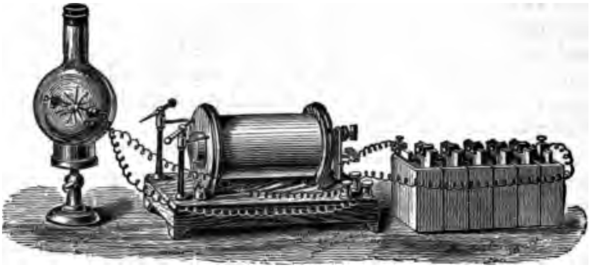

FIG. 19.

Nitric Acid, or Hydrogen Nitrate.

Symbol HNO_3, *Molecular Weight* 62·89.—Nitre, or potassium nitrate, is generally formed by the gradual oxidation of nitrogenous animal matter in presence of the alkali potash. Spring water, especially the surface well-water of towns, frequently contains nitrates in solution, owing to water passing through soil containing decomposing animal matter, which by oxidation yields nitrates. For this reason, water containing nitrates is unfit for drinking purposes. Potassium nitrate, KNO_3 (commonly called saltpetre), occurs as an incrustation on the soil in various localities, especially in India;

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[1] For a test distinguishing ozone from the oxides of nitrogen see p. 17.

and sodium nitrate, $NaNO_3$, or Chili saltpetre, is found in large beds on the coast of Chili and Peru. Nitric acid is obtained by heating nitre, KNO_3, or Chili saltpetre, $NaNO_3$, with sulphuric acid (or hydrogen sulphate), H_2SO_4; when nitric acid, HNO_3, and hydrogen potassium sulphate, $HKSO_4$, are formed. The decompositions here effected may serve as a type of a very large number of chemical changes classed as *double decompositions.* These may be all represented as consisting in an exchange between two elements, or groups of elements; thus, in the case in question, one atom of the hydrogen in sulphuric acid changes place with one atom or its *equivalent* of potassium in the nitre. These double decompositions may be represented in the form of an equation, in which one side signifies the arrangement and relative weights of the elements *before* combination, the other the arrangement and relative weights of the same elements *after* the chemical change has taken place, thus—

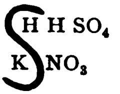
$$KNO_3 + H_2SO_4 \quad = \quad HNO_3 \qquad + \quad HKSO_4 \text{ or,}$$

Nitre and Sulphuric Acid give Nitric Acid and Hydrogen Potassium Sulphate.

The relative weights of the elements and compounds entering into the decomposition are easily ascertained when we remember that each symbol expresses not merely the nature of the element, but also the relative weight with which it combines, and that the combining weight of a compound is the sum of the combining weights of its constituents. The numbers expressed by the above equation, taking the nearest whole numbers for the sake of simplicity, are

$$\begin{array}{c}
K \quad N \quad O_3 + H_2 \; S \quad O_4 = H \quad N \quad O_3 + H \quad K \quad S \quad O_4 \\
39 + 14 + 48 + 2 + 32 + 64 = 1 + 14 + 48 + 1 + 39 + 32 + 64 \\
101 \qquad + \qquad 98 \quad = \quad 63 \quad + \quad 136
\end{array}$$

We may express these double decompositions perhaps more clearly if we represent by a curved line the actual exchange of hydrogen for potassium, thus—



or by a straight line, thus—

$$\begin{array}{r|l}
H & HSO_4 \\
NO_3 & K
\end{array}$$

This signifies that, if we require 63 parts by weight of nitric acid, we shall require to take 101 parts of nitre and 98 parts of sulphuric acid, and that we shall have 136 parts of hydrogen potassium sulphate formed. Knowing these numbers, it is easy to calculate the proportions of ingredients needed to produce any given quantity of nitric acid.

Nitric acid is prepared on a small scale by placing about equal weights of nitre and sulphuric acid in a stoppered retort, which is gradually heated by a Bunsen burner, as in Fig. 20, p. 63: the nitric acid formed distils over, and may be collected in a flask cooled with water. To prepare it on the large scale Chili saltpetre is mixed with sulphuric acid, the mixture heated in iron cylinders, and the nitric acid, which distils over, collected in stoneware bottles. Only half the amount of sulphuric acid required according to the above equation is employed, as at the higher temperature reached in the process the sodium hydrogen sulphate first formed acts on more Chili saltpetre according to the following equation:

$$NaHSO_4 + NaNO_3 = Na_2SO_4 + HNO_3.$$

The two different equations representing the two reactions may also be represented in one, as follows:

$$2NaNO_3 + H_2SO_4 = Na_2SO_4 + 2HNO_3.$$

Nitric acid thus obtained is represented by the formula HNO_3; it is a strongly fuming liquid, colourless when pure, but usually slightly yellow from the presence of lower oxides of nitrogen. It was formerly termed *aqua fortis*. Its specific gravity is 1·51 at 18°; it does not possess a constant boiling point, as it gradually undergoes decomposition by boiling, and becomes weaker: if mixed with water, and distilled under the ordinary atmospheric pressure, the residual acid is found at last to attain a fixed composition, boiling constantly at 120°·5, containing 68 per cent. of HNO_3, and possessing a specific gravity of 1·414. When mixed with less water, a stronger acid than this comes over; when mixed with more water, a weaker one first distils over till this constant composition is attained. Nitric acid contains 76 per cent. of oxygen, with some of which it easily parts; hence it acts as a strong oxidising agent. This is seen when we bring a

small quantity of metallic copper or tin into this liquid diluted with a little water; red fumes are immediately given off, and the metals are oxidised; for the same reason nitric acid bleaches indigo solution, oxidising, and therefore destroying, the colouring matter. This reaction, and the formation of red fumes in presence of metallic copper, &c., serve as modes of detecting the presence of nitric acid. One of the most delicate tests for this acid consists in adding to the liquid to be tested an equal volume of strong sulphuric acid, cooling the mixture well, and carefully pouring on to its surface a solution of ferrous sulphate, $FeSO_4$: if any nitric acid be present a black ring is produced where the two layers of liquid meet. Nitric acid forms, with metallic oxides, by the process of double decomposition, a numerous family of salts called nitrates: these are nearly all soluble in water, and many of them are largely used in the arts for various purposes. They will be mentioned under the several metals.

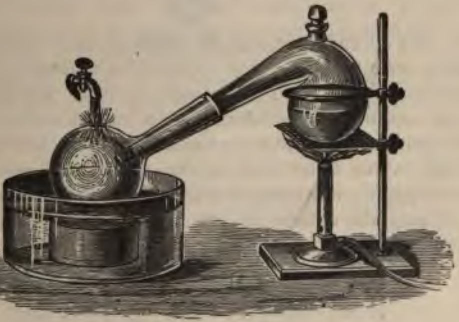


FIG. 20.

Nitric acid itself is largely employed in the preparation of gun cotton, nitro-glycerine, colouring matters, &c.

Acids, Bases, and Salts.—In nitric acid we have the first example of a series of important compounds known as *acids.* Most of the acids are soluble in water; they possess a sour taste, and have the property of turning blue litmus-solution red. All acids contain hydrogen, combined either with an element, or with a group of elements, which almost always

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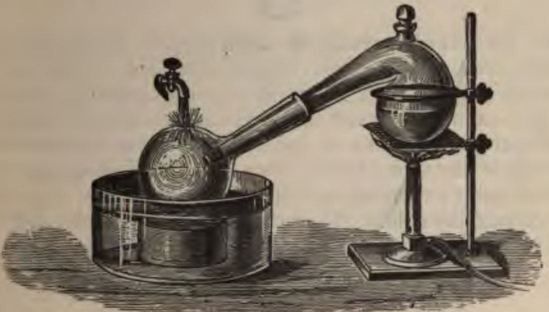

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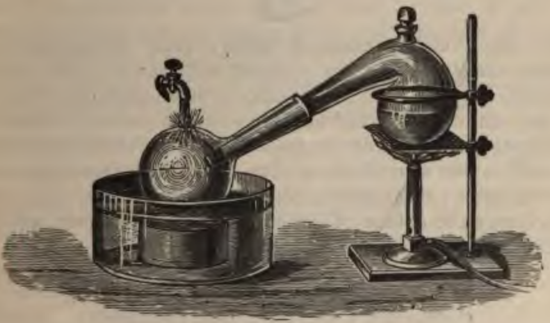

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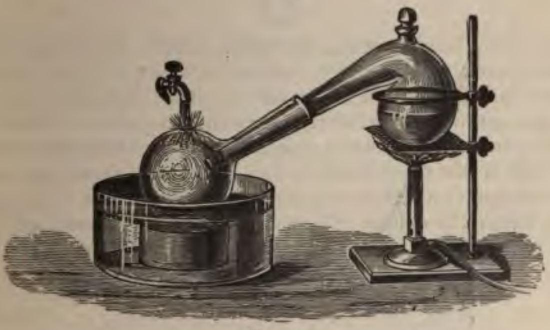

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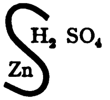
Nitric acid itself is largely employed in the preparation of gun cotton, nitro-glycerine, colouring matters, &c.

Acids, Bases, and Salts.—In nitric acid we have the first example of a series of important compounds known as *acids.* Most of the acids are soluble in water; they possess a sour taste, and have the property of turning blue litmus-solution red. All acids contain hydrogen, combined either with an element, or with a group of elements, which almost always contains oxygen; in the latter case the substances are termed *oxy-acids*. These acids may be regarded as water, $\left.\begin{matrix}H\\H\end{matrix}\right\}O$, in which part of the hydrogen is replaced by the oxygenated group of atoms: thus nitric acid may be represented as $\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$. When the rest of the hydrogen of an acid is replaced by a metal, as, for instance, when sulphuric acid acts upon zinc, the acid character of the substance disappears, and a *salt*, called zinc sulphate, is formed, thus—



Salts are likewise produced when certain hydroxides and oxides are brought into contact with acids; thus if the solution of potassium hydroxide (caustic potash), obtained by the action of the metal potassium on water, is added to nitric acid, the alkaline or caustic properties of the hydroxide as well as the sour taste of the nitric acid disappear at a certain point; the solution becomes *neutral*, that is it does not change the colour of either blue or red litmus, and the salt potassium nitrate is contained in the liquid: thus—

$$\left.\begin{matrix}H\\K\end{matrix}\right\}O + \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}NO_2\\K\end{matrix}\right\}O.$$

The soluble hydroxides which thus act upon acids are termed *alkalis*, and have the power of turning red litmus-solution blue. In the same way many metallic oxides, called *basic oxides*, or *bases*, act upon acids to form salts; thus silver oxide dissolves in nitric acid, and neutralises its acid character, forming soluble silver nitrate, thus—

$$\left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O + 2\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + 2\left.\begin{matrix}NO_2\\Ag\end{matrix}\right\}O.$$

Nitrogen Pentoxide, or Nitric Anhydride.[1]

Symbol N_2O_5, or $\left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O$:—This oxide of nitrogen can be prepared directly from pure nitric acid by carefully adding to it phosphorus pentoxide, which takes away one molecule of water from two of nitric acid, thus—

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[1] By an anhydride is meant an oxide which forms an acid on treatment with water.

$$2HNO_3 = N_2O_5 + H_2O.$$

Another method of preparing this substance is to pass dry chlorine gas over silver nitrate; silver chloride is formed, oxygen is given off, and a white crystalline substance produced, which on analysis is found to be nitrogen pentoxide. The reaction is represented by the equation:—

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O.$$

Nitrogen pentoxide melts at + 30° and boils at + 45°; it very easily undergoes decomposition, and unites with great energy with water, forming nitric acid.

All the other oxides of nitrogen may be obtained from nitric acid by depriving it of its hydrogen, and more or less of its oxygen.

LESSON VII.

Nitrogen Monoxide, or Nitrous Oxide.

Symbol N_2O, *Molecular Weight* 43·98, *Density* 21·99, is obtained by heating ammonium nitrate, NH_4NO_3 or $\left.\begin{matrix}NH_4\\NO_2\end{matrix}\right\}O$, in a flask such as that used for the production of oxygen, and is best collected over warm water (see Fig. 21). The salt decomposes on heating as follows: $NH_4NO_3 = N_2O + 2H_2O$; or ammonium nitrate yields nitrogen monoxide and water. Nitrous oxide is a colourless inodorous gas possessing a slightly sweet taste; it is somewhat soluble in cold water, one volume of water at 0° dissolving 1·305 volumes of the gas, whilst one volume of water at 24° dissolves only 0·608 volume. Nitrogen monoxide like all the other gases, liquefies when exposed either to great pressure or to a great degree of cold. Thus, if it be brought under a pressure of about 30 atmospheres at 0°, or if it be cooled down to - 88° under the ordinary pressure, it forms a colourless liquid; (in other words, the tension of nitrous oxide vapour or gas is 1 atmosphere at - 88°, and 30 atmospheres at 0° C.). If this liquid be cooled below - 115°, it solidifies to a transparent mass. By the rapid evaporation of this liquid in a vacuum, a reduction of temperature to - 140° C. is obtained. A glowing chip of wood when plunged into nitrous oxide rekindles, and the wood continues to burn with a brighter flame than in the air, whilst phosphorus on burning in this gas evolves nearly as much light as in pure oxygen; a feeble flame of sulphur is, however, extinguished on bringing it into the gas, but if burning strongly it also continues to burn brightly. This is owing to the fact that the gas must be decomposed into nitrogen (1 volume) and oxygen (half a volume) before bodies can burn in it; and to effect this decomposition a tolerably high temperature is necessary—the same products of combustion being produced as if the combustion went on in the air. When inhaled for some time it produces insensibility, and is much used in dental operations. If it is mixed with air, it produces a peculiar intoxicating effect on the human frame; hence it has been called *laughing-gas*. The composition of nitrous oxide may be determined as follows: a bent tube

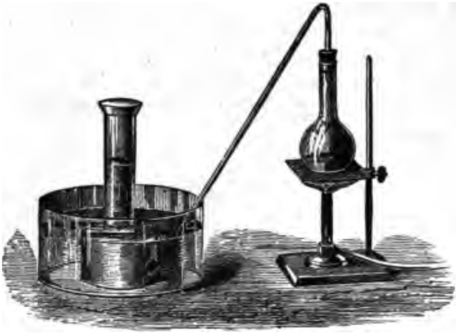


FIG. 21.

(Fig. 22) is filled with the dry gas over mercury up to a certain mark on the tube, a small pellet of metallic potassium having been previously introduced into the bent part of the tube; this is then heated by a spirit-lamp, or Bunsen's burner, while the open end of the tube is closed with the thumb under the mercury, to prevent a loss of gas by the sudden expansion caused by the combustion. The potassium burns in the gas, uniting with the oxygen to form solid potassium oxide, whilst the nitrogen remains in the tube. On removing the thumb and allowing the tube to cool, it will be seen that the volume of nitrogen is exactly the same as the volume of nitrous oxide taken; hence this gas contains its own volume of nitrogen. But we know by experiment that the weight of one volume of the gas is 21·99, so that if we subtract from this the weight of one volume of nitrogen (viz. 14·01) we shall obtain the weight of oxygen (7·98) contained in one volume of nitrogen monoxide. Hence we see that two volumes of nitrous oxide are composed of two volumes of nitrogen and one volume of oxygen, or 43·98 parts by weight contain 28·02 of nitrogen and 15·96 of oxygen, and its formula is therefore N_2O. The specific gravity of nitrous oxide (air = 1) is 1·527: 1,000 cc. at 0° and 760 mm. weigh 1·972 grams.

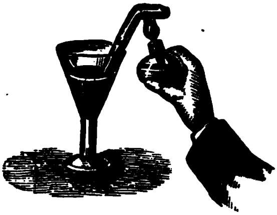


FIG. 22.

Nitrogen Dioxide or Nitric Oxide.

Symbol NO, *Molecular Weight* 29·97, *Density* 14·98.—A colourless gas obtained by acting upon copper turnings with nitric acid. The arrangement for preparing this gas and collecting it over water are shown in Fig. 23.

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

Copper and nitric acid give copper nitrate, nitrogen dioxide, and water.

Nitric oxide when cooled to − 11° under a pressure of 104 atmospheres condenses to a liquid. When the gas is mixed with oxygen it combines directly with this latter gas, forming red fumes consisting of a mixture of nitrogen trioxide, N_2O_3, and nitrogen peroxide, NO_2, which are readily soluble in water, and by this property it may be distinguished from all other gases. Although nitric oxide contains half its volume of oxygen, and more oxygen in proportion by weight than nitrous oxide, it does not easily support combustion, as it requires a high temperature for its decomposition; thus ignited phosphorus, unless burning very brightly, is extinguished on plunging it into nitric oxide gas.

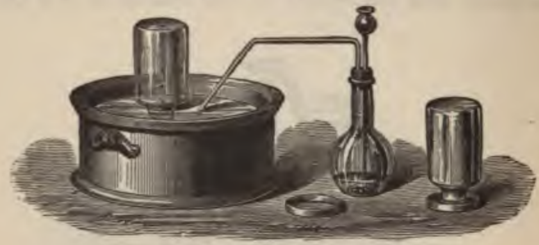


FIG. 23.

The composition of this gas may be determined according to the method described under nitrogen monoxide: one volume of nitrogen dioxide yields half a volume of nitrogen; as the weight of one volume of nitrogen dioxide is 14·98, the weight of oxygen contained in one volume of this gas is 14·98 − 7 = 7·98: or two volumes of nitrogen dioxide weigh 29·97, and are composed of one volume of nitrogen weighing 14·01, and one of oxygen weighing 15·96. Hence, in accordance with the law mentioned on pp. 57, 158, respecting the densities of compound gases, the formula of this oxide should be NO and not N_2O_2.

The specific gravity of nitric oxide (air = 1) is 1·038, and 1,000 cc. of this gas at 0° and 760 mm. weigh 1·343 grams.

Nitrogen Trioxide.

Symbol N_2O_3, *Molecular Weight* 75·9, *Density* 37·95.—This substance is prepared by mixing four volumes of dry nitrogen dioxide with one volume of oxygen, and cooling the mixture to − 18°; the two gases combine to form red fumes, which condense to a volatile indigo-blue coloured liquid; the same blue body is obtained by adding water to nitrogen tetroxide and drying the distillate over calcium chloride. It is also formed by the action of moderately strong nitric acid upon arsenic trioxide, with formation of arsenic acid, thus:

$$As_2O_3 + 2HNO_3 + 2H_2O = N_2O_3 + 2H_3AsO_4.$$

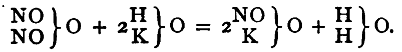
Arsenic trioxide, nitric acid and water, yield nitrogen trioxide and arsenic acid.

Nitrous Acid.

Symbol HNO_2. Nitrogen trioxide dissolves in ice-cold water, forming a blue liquid, and containing nitrous acid or hydrogen nitrite, HNO_2, in solution; this compound is very unstable, and decomposes when the water is warmed into nitric acid and nitric oxide, thus:

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

The salts formed by nitrous acid are, however, not liable to such easy decomposition; potassium nitrite, KNO_2 is obtained by heating potassium nitrate, KNO_3, which loses one atom of oxygen; the same salt is produced when nitrogen trioxide is led into a solution of caustic potash, thus:



$$\left.\begin{matrix}NO\\NO\end{matrix}\right\}O + 2\left.\begin{matrix}H\\K\end{matrix}\right\}O = 2\left.\begin{matrix}NO\\K\end{matrix}\right\}O + \left.\begin{matrix}H\\H\end{matrix}\right\}O.$$

Hence, nitrogen trioxide stands to the nitrites in the same position as nitrogen pentoxide to the nitrates. It will be noticed that nitr*ic* acid forms salts called nitr*ates*, whilst nitr*ous* acid gives rise to nitr*ites*; this is an example of a general rule adopted in chemical nomenclature that if the specific name of an acid or hydrogen salt end in "ous," the names of the corresponding metallic salts end in "ite," whilst acids whose names end in "ic" form salts ending in "ate."

Hyponitrous Acid.

An acid has been obtained which stands to nitrous oxide, N_2O, as nitrous acid does to nitrogen trioxide. To this substance the name of *hyponitrous acid* has been given, and its formula is HNO or $H_2N_2O_2$: it is however not known to exist in the free state, although its sodium compound NaNO can be prepared by the action of sodium amalgam on a solution of sodium nitrate

$$NaNO_3 + 2H_2 = NaNO + 2H_2O.$$

Nitrogen Peroxide.

Symbol NO_2, *Molecular Weight* 45·93, *Density* 22·96.—This substance forms the greater part of the reddish-brown fumes evolved when nitric oxide gas escapes into the air; it is, however, best prepared by heating lead nitrate in a hard glass retort; lead oxide, oxygen, and nitrogen peroxide are produced by the decomposition of the nitrate, thus:

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Nitrogen peroxide, NO_2, solidifies at $-9°$ to long prisms; these on fusing yield a yellow liquid, boiling at 22°. At a low temperature it has probably the formula N_2O_4, but at a higher temperature it has the density 22·96, and its formula must then be NO_2, the molecules of N_2O_4 having split up into two of NO_2.

NITROGEN AND HYDROGEN.

Ammonia.

Symbol NH_3, *Molecular Weight* 17·01, *Density* 8·5.—Nitrogen and hydrogen form three compounds, the most important of which is Ammonia.

This substance is chiefly obtained from the decomposition of animal or vegetable matter containing nitrogen and hydrogen, being formed either gradually at the ordinary temperature, or quickly under the influence of heat: thus when horn, hide, or coal, is heated, ammonia is given off; hence ammonia was known as *spirit of hartshorn*. The name ammonia is derived from the fact that a compound containing ammonia, called sal-ammoniac, was first prepared by the Arabs in the deserts of Libya, near the temple of Jupiter Ammon, by heating camels' dung. Guano, the dried excrement of sea-birds, and the urine of animals, likewise contain large quantities of ammonia. Ammonia and its compounds are now, however, mainly obtained from the ammoniacal liquors of the gasworks: coal contains about 2 per cent. of nitrogen, which, when the coal is heated in closed vessels, largely comes off in combination with the hydrogen of the coal as ammonia. Hydrochloric acid is added to this ammoniacal liquor, and the solution evaporated, when the sal-ammoniac of commerce is obtained.

Ammonia may also be formed by the action of nascent hydrogen on dilute nitric acid; and when this acid is placed in contact with metallic zinc or iron, ammonia is formed, thus:

$$9HNO_3 + 4Zn = 4Zn(NO_3)_2 + 3H_2O + NH_3.$$

Ammonia gas is best prepared by heating in a glass flask one part by weight of sal-ammoniac, or ammonium chloride, NH_4Cl, and an excess, or two parts by weight of powdered quicklime. The decomposition which here occurs is represented by the following equation:

$$CaO + 2NH_3HCl = CaCl_2 + 2NH_3 + H_2O.$$

Quicklime and sal-ammoniac give calcium chloride, ammonia, and water.

Ammonia gas is colourless, and possesses a most pungent and peculiar smell, by means of which it can be readily recognized; it is lighter than air, its specific gravity (air = 1) being 0·59, and it may be collected by displacement, the neck of the bottle intended to receive the gas being turned downwards, as in Fig. 24. A cylinder filled with quicklime is here placed between the flask and the bottle for the purpose of completely drying the ammonia. A simpler arrangement is shown in Fig. 25; a layer of powdered quicklime placed in the upper part of the flask itself serves to dry the gas. Ammonia may also be collected over mercury, but not over water, as it is extremely soluble in this liquid, one gram of water at 0° absorbing 0·875 gram, or 1148 times its volume, of ammonia, under a pressure of 760 mm.; whilst at 20° the same weight of water absorbs 0·526 gram, or 741·24 times its volume, under the same pressure. The solution of ammonia gas in water is the common *liquor ammoniæ* of the shops, which has a specific gravity of about 0·880. Ammonia gas, as well as the aqueous solution, possesses a strong alkaline reaction, turning red vegetable colours blue; it unites with the most powerful acids, forming compounds called the salts of ammonium (see p. 199), which closely resemble the salts of the alkali-metals; hence the name of the volatile alkali has been given to ammonia. The action of ammonia gas on nitric acid may be thus represented—

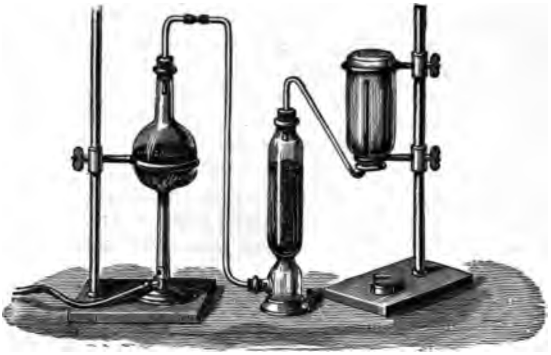


FIG. 24.

$$NH_3 + NO_3H = NH_4NO_3\,;\ \text{or}\ \left.\begin{matrix}NH_4\\NO_2\end{matrix}\right\}O.$$

On exposure to a pressure of seven atmospheres at the ordinary temperature of the air (about 15° C.), ammonia condenses to a colourless liquid, boiling at $-33°{\cdot}7$; and this liquid, if cooled below −75°, freezes to a transparent solid. An elegant application of the principle of the latent heat of vapours has recently been made in the case of ammonia in M. Carré's freezing machine (Fig. 26). This consists essentially of two strong iron vessels connected in a perfectly air-tight manner by a bent pipe; one of these vessels contains an aqueous solution of ammonia saturated with the gas at 0°. When it is desired to procure ice, the vessel (A) containing the ammonia solution (which we will term the retort) is gradually heated over a large gas-burner, the other vessel B (the receiver) being placed in a bucket of cold water: in consequence of the increase of temperature, the gas cannot remain dissolved in the water, and passes into the receiver, where, as soon as the pressure amounts to about 10 atmospheres, it condenses in the liquid form. When the greater part of the gas has thus been driven out of the water, the apparatus is reversed, the retort (A) being cooled in a current of cold water, whilst the liquid it is desired to freeze is placed in the interior of the receiver (B). A re-absorption of the ammonia by the water now takes place, and a consequent evaporation of the liquefied ammonia in the receiver: this

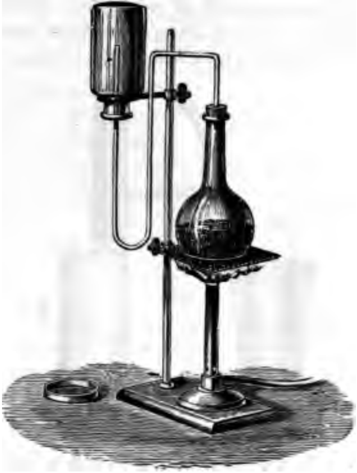


FIG. 25.

evaporation is accompanied by an absorption of the heat which is necessary for the existence of the gas; hence the receiver is soon cooled far below the freezing point, and ice is produced around it.

The composition of ammonia may be ascertained by leading the gas through a red-hot tube, or passing a series of electric sparks through the gas, when it will be decomposed into nitrogen and hydrogen, which will be found to occupy together a volume twice as large as the ammonia taken, and mixed together in the proportions of three volumes of hydrogen to one volume of nitrogen. That this is the case may be proved by exploding the mixed gases with $\frac{3}{8}$ of their volume of oxygen, when the whole of the hydrogen will unite to form water, and pure nitrogen will be left. Hence the formula NH_3 is given to the gas. A mode of exhibiting the presence of hydrogen is to apply a light to the end of a red-hot tube through which the ammonia is passing; the hydrogen which is thus set free takes fire and burns with formation of water. Pure nitrogen may be obtained from the mixed gases by passing them over red-hot oxide of copper, when water is formed, and the remaining nitrogen gas may be collected over the pneumatic trough.

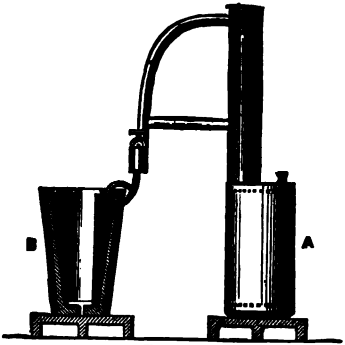


FIG. 26.

The salts of ammonia are described together with those of potassium and sodium (p. 185).

Up to the year 1887, ammonia was the only known compound of nitrogen and hydrogen; since then two other have been discovered, both of which are obtained as products of decomposition of compounds containing carbon and nitrogen.

Hydrazine or *Diamide*, $H_2N.NH_2$ is prepared by boiling triazoacetic acid (p.) with sulphuric acid; it combines with the latter forming the salt, *hydrazine sulphate*, N_2H_4, H_2SO_4. Free hydrazine is a gas with a peculiar penetrating odour, which has not been obtained in the pure condition, as it combines with great avidity with water forming *hydrazine hydrate*, $N_2H_4.H_2O$. This is prepared by boiling the sulphate with caustic soda solution, and forms a refractive, somewhat oily fuming liquid, boiling at 118·5°, and having a most corrosive action, attacking even glass. It solidifies at a very low temperature, and has a sp. gr. of 1·03 at 21°. It possesses also the property of precipitating many metals from solutions of their salts.

Hydrazine combines with a large number of acids, forming a well defined series of salts.

Azoimide, N_3H.—This compound is obtained from benzoyl-diazoimide (see *Organic Chemistry*), and has the composition N_3H. It is a colourless mobile liquid, boiling at 37°, and having a very pungent and exceedingly unpleasant smell. It is very unstable and frequently decomposes with a tremendous explosion. It mixes with water and alcohol in all proportions, and unites with bases forming salts just in the same manner as hydrochloric acid (p. 100). Thus with caustic soda it gives the *sodium* salt N_3Na, and with ammonia the *ammonium* salt $N_3.NH_4$ or N_4H_4. These salts are also very explosive.

LESSON VIII.

CARBON.

Symbol C, *Atomic Weight* 11·97.—Carbon is the first solid element which we have had to notice; it is not known either as a liquid or as a gas. Carbon is remarkable as existing in three distinct forms, which, in outward appearance or physical properties, have nothing in common, whilst their chemical relations are identical. These three *allotropic* forms of carbon are (1) Diamond, (2) Graphite or Plumbago, (3) Charcoal: these substances differ in hardness, colour, specific gravity, &c., but they each yield on combustion in the air or oxygen the same weight of the same substance, carbonic acid, or carbon dioxide;[1] 11·97 parts by weight of each of these forms of carbon yielding 43·98 parts by weight of carbon dioxide. Carbon is the element which is specially characteristic of animal and vegetable life, as every organized structure, from the simplest to the most complicated, contains carbon: if carbon were not present on the earth, no single vegetable or animal body such as we know could exist. In addition to the carbon which is found free in these three forms, and that contained combined with hydrogen and oxygen in the bodies of plants and animals, it exists combined with oxygen as free carbon dioxide in the air, and with calcium and oxygen as calcium carbonate in limestone, chalk, marble, corals, shells, &c. The fact has already been noticed that plants are able, when exposed to sunlight, to decompose the carbon dioxide in the air, liberating the oxygen, and taking the carbon for the formation of their vegetable structure; whilst all animals, living directly or indirectly upon vegetables, absorb oxygen, and evolve carbon dioxide. Thus the sun's rays, through the medium of plants, effect deoxidation or reduction, while animals act as oxidizing agents with respect to carbon. It must, however, be remembered that this decomposition of carbon dioxide by plants is a nutritive and not a respiratory process.

The element carbon not only combines directly with oxygen, but also with hydrogen, forming a compound called acetylene, C_2H_2. With oxygen, hydrogen, and nitrogen, carbon forms a series of more or less complicated compounds very much more extended than the series formed with these bodies by any other element. The properties of most of these compounds, owing to their complexity, are best considered in a separate chapter, under the head of organic chemistry. Hence it will be better to postpone till then the consideration of several of the properties of carbon. Some of the simpler compounds are, however, for the sake of convenience usually considered with the inorganic compounds.

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[1] Although the term "acid," as we have already seen, strictly denotes a hydrogen salt, yet the word has been applied so long to a few other compounds containing no hydrogen, such as carbon dioxide, &c., that these bodies are universally known by the names carbonic acid, &c. Another term for this compound is carbonic anhydride.

The Diamond was first proved to consist of carbon by Lavoisier, in 1775-6, by burning it in oxygen, and collecting the carbon dioxide formed; it occurs crystallized in certain sedimentary rocks and gravel in India (Golconda), Borneo, the Cape, and the Brazils. Diamond occurs crystallized in forms (Fig. 27), derived by a symmetrical geometric operation from a regular octahedron, belonging to the regular system of Crystallography (see p. 179). The specific gravity of diamond varies from 3·5 to 3·6; it is the hardest of all known bodies, and when cut possesses a brilliant lustre, and a high refractive power. In addition to its employment as a gem, the diamond is used for cutting and writing upon glass. We are altogether unacquainted with the mode in which the diamond has been formed: it has, however, probably not been produced at a high temperature, because, when heated strongly in a medium incapable of acting chemically upon it, the diamond swells up, and is converted into a black mass resembling coke.

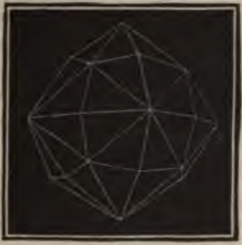

FIG. 27.

Graphite, or *Plumbago*, crystallizes in six-sided plates which have no relation to the form in which the diamond crystallizes. Graphite occurs in the oldest sedimentary formations, and in granitic or primitive rocks; it is found in Borrowdale in Cumberland, and in large quantities in North

America, Siberia, and Ceylon. It has a black metallic appearance (whence the familiar name, black lead), and leaves a mark when drawn over paper. The specific gravity of graphite is 2·15 to 2·35. Coarse impure graphite may be purified by heating the powder with sulphuric acid and potassium chlorate; a compound is thus obtained which, on being heated strongly, decomposes, leaving pure graphite as a bulky and finely-divided powder: this powder when strongly compressed forms a coherent mass, from which pencils and other articles can be made. Graphite is used for polishing surfaces of ironwork, and also for giving a protecting varnish to grains of gunpowder. Graphite is also produced in the manufacture of iron; it occasionally separates from the molten pig-iron in the form of scales.

Charcoal is the third allotropic modification of carbon. It is obtained in a more or less pure state whenever animal or vegetable matter is heated to redness in a vessel nearly closed: the volatile matters (compounds of carbon, hydrogen, and oxygen) are thus driven off, and the residue of the carbon, together with the ash or mineral portion of the organism, remains behind.

The purest form of charcoal-carbon is found in lampblack; it also occurs as wood charcoal, coal, coke, and animal charcoal. This form of carbon does not crystallize, and is hence termed *amorphous* carbon: it is much lighter than either of the other two forms, the specific gravity of powdered coke varying from 1·6 to 2·0. Charcoal appears at first sight to be lighter than water, as a piece of it floats on the surface of this liquid; this is, however, due to the porous nature of the charcoal, for if it be finely powdered it sinks to the bottom of the water. This porous nature of charcoal enables it to exert a remarkable absorptive power, of which much use is made in the arts. Charcoal is thus able to absorb about ninety times its own volume of ammonia gas, and about nine volumes of oxygen. In the process of sugar-refining, use is made of the property of charcoal to absorb the colouring matters present in the raw sugar: the kind of charcoal best suited to this purpose is that obtained by heating bones in a closed vessel. Charcoal is also used as a disinfectant in hospitals and dissecting rooms, &c. It appears that the putrefactive gases when absorbed by the charcoal undergo a gradual oxidation from contact with the oxygen of the air taken up by the charcoal, and are thus rendered harmless.

Coal is a form of carbon less pure than wood charcoal. It consists of the remains of a vegetable world which once flourished on the earth's surface: the original woody fibre has undergone a remarkable transformation in passing into coal, having been subjected to a process similar, from a chemical point of view, to that by which wood is transformed into charcoal. It has not, however, lost the whole of its hydrogen and oxygen, and it has at the same time become bitumenized, so that for the most part all the vegetable structure has disappeared. There are many different kinds of coal, containing more or less of the oxygen and hydrogen of the original wood: cannel coal and boghead coal contain the most hydrogen, and anthracite coal the least. The alteration in composition which wood has undergone in passing into the various forms of coal is seen from the following table:—

Compositions of Fuels (ash being deducted).

Description of Fuel.	Percentage Composition.		
	Carbon.	Hydrogen.	Nitrogen and Oxygen.
1 Woody Fibre	52·65	5·25	42·10
2 Peat from the Shannon	60·02	5·88	34·10
3 Lignite from Cologne	66·96	5·24	27·76
4 Earth Coal from Dax	74·20	5·89	19·90
5 Wigan Cannel	85·81	5·85	8·34
6 Newcastle Hartley	88·42	5·61	5·97
7 Welsh Anthracite	94·05	3·38	2·57

COMPOUNDS OF CARBON WITH OXYGEN.

Carbon forms two compounds with oxygen, viz.:

Carbon Monoxide, or CO.
Carbon Dioxide, or CO_2.

Carbon Dioxide or *Carbonic Anhydride* (commonly called *Carbonic Acid*).

Symbol CO_2, *Molecular Weight* 43·89, *Density* 21·94.—Carbon dioxide is always formed when carbon is burnt in excess of air or oxygen. It is best prepared by acting upon marble, chalk, or other form of calcium carbonate, with hydrochloric acid. On pouring some of this acid upon pieces of marble contained together with some water in a flask, a rapid effervescence from the disengagement of carbon dioxide gas at once occurs, calcium chloride being left behind in solution in the flask. Fig. 28 shows the mode of collecting this gas by displacement of the air. The decomposition is thus represented:

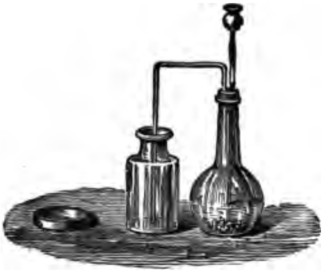

FIG. 28.

$$CaCO_3 + 2HCl = CO_2 + H_2O + CaCl_2.$$

Calcium carbonate and hydrochloric acid give carbon dioxide, water, and calcium chloride.

Carbon dioxide occurs free in the air, and in the water of many mineral springs. The quantity of this gas present in the air is nearly constant, and amounts to from 3 to 4 volumes per 10,000 of air: this quantity, though relatively small, is, taken altogether, very large, being about 3 billions of tons in weight, as can be easily calculated if we know the weight of the atmosphere and the density of carbonic acid.

It is also evolved in very large quantities from the craters of active volcanoes, as well as from fissures in the districts of extinct volcanic action.

Owing to the evolution of carbon dioxide in respiration and in the burning of coal-gas, &c., this gas is always found in larger quantities in dwelling-rooms than in the open air. When the air of a room contains 0·10 per cent. of this gas, it is certainly unfit for continued respiration, not only on account of the deleterious effects produced by carbon dioxide, but also because, together with this gas, volatile putrescible matters are given off from the skin and lungs of animals, and these matters act in a prejudicial manner upon the health; hence the necessity for attention to the ventilation of dwelling-rooms and public buildings. Carbon dioxide gas is also given off in the process of fermentation; it occurs frequently at the bottom of old wells, and forms the *choke-damp*, or *after-damp*, of the coal mines. Compounds of carbon dioxide with lime or magnesia, such as limestone or calcium carbonate, $CaCO_3$, and magnesian limestone, &c., occur plentifully in nature, sometimes forming whole mountain chains. Calcium carbonate also constitutes the main portion of coral, a substance of which whole continents are being built up in the Pacific Ocean.

Carbon dioxide gas is colourless and inodorous, but possesses a slightly acid taste; it is 1·529 times heavier than air, and is tolerably soluble in water, but is all expelled by boiling, one volume of water at 0° dissolving in 1·797 volumes of this gas, whilst at 20° only 0·901 volume is absorbed. The volume of this gas absorbed by water at the same temperature is found to remain the same, under whatever pressure the gas may be measured. As the volumes occupied by any given quantity of gas measured under different pressures vary inversely as these pressures, it is clear that the weights of carbon dioxide thus absorbed must be proportional to the pressures. Thus, for instance, under the pressure of 1 atmosphere and at the ordinary temperature of the air 1 cc. of water dissolves 1 cc. or 1·972 milligrams of carbon dioxide. So under a pressure of 2 atmospheres 1 cc. of water will at the same temperature dissolve *1* cc. (measured under the pressure of 2 atmospheres) or 2 × 1·972 = 3·944 milligrams of carbon dioxide. The increased quantity of absorbed carbonic acid under increased pressure is seen when a bottle of soda-water or champagne is opened; the pressure being diminished by removal of the cork, a brisk effervescence and escape of the dissolved gas occurs. The same relation is found to hold good when many other gases are dissolved in water under varying pressures.

The aqueous solution of carbon dioxide reddens blue litmus-paper, and when placed in contact with a metallic oxide, as for example calcium oxide or lime, CaO, gives rise to the formation of salts such as calcium carbonate; this aqueous solution may be considered to contain a true acid, the real carbonic acid, H_2CO_3 (which, however, has never yet been isolated), and the reaction which then takes place may be thus represented:

$$H_2CO_3 + CaO = CaCO_3 + H_2O.$$

Carbonic acid and calcium oxide give calcium carbonate and water.

The red colour produced by the acid on litmus-paper disappears on drying, owing to the decomposition of this true carbonic acid into carbon dioxide and water, thus:

$$H_2CO_3 = CO_2 + H_2O.$$

Carbon dioxide gas does not support the combustion of bodies in general, such as wood, sulphur, or phosphorus; but certain metals—for instance potassium and magnesium —heated in the gas, are able to decompose it, burning in it, and uniting with the oxygen to form oxides, while the carbon is liberated.

Carbon dioxide can be condensed to a liquid by the application of great pressure, or by cooling the gas to a low temperature: liquid carbon dioxide is a colourless and very mobile liquid, which is remarkable inasmuch as it expands by heat more than the gaseous form of the same substance, 100 volumes of this liquid at 0° becoming 106 volumes at 10, while 100 volumes of the gas at 0° must be heated to 16°·4 before they expand to 106 volumes; hence this body is an exception to the rule that liquids expand by heat less than gases, and at the same time forms an excellent illustration of the fact, that liquids expand proportionally much more when submitted to a high pressure than when under a low one: thus, the expansion of water above 100° is much greater than that below 100°. The boiling-point of liquid carbon dioxide is −78°. At a still lower temperature it freezes to a colourless, ice-like solid. At 0° the tension of its vapour is 35·5 atmospheres; and at 30°, 73·5 atmospheres. The liquefaction of carbon dioxide gas can be effected by evolving the gas in a strong closed vessel, so that it is either condensed by its own pressure, as is the case with ammonia in Carré's freezing-machine (described on p. 73); or by pumping the gas by means of an ordinary forcing syringe into a strong wrought-iron receiver, kept during the process at a temperature of 0°. As soon as the volume of gas pumped in amounts to about 36 times the volume of the receiver, each stroke of the syringe produces a condensation of the gas which is pumped in; and thus the receiver can easily be filled with liquid. If the stopcock be then opened so that the liquid is forced out, a portion at once assumes the gaseous state; and so much heat is absorbed by this sudden transition from the liquid to the gaseous form, that a portion of the liquid is solidified and deposited in the form of white, snow-like flakes, which can be collected by allowing the stream of liquid to flow into a thin brass box with perforated sides.

Solid carbon dioxide thus obtained is a light, snow-like substance, which, owing to the bad conducting power for heat of the gas which the solid substance is constantly giving off, may be handled without damage, although its temperature is below −78° C. If, however, the solid be forcibly pressed between the fingers, so that the substance really comes in contact with the skin, a sharp pain will be felt, and a blister like one produced by touching a hot iron will be caused. This solid carbon dioxide is much used for the production of very low temperatures; for this purpose it is mixed with ether, and the mixture brought into the vacuum of an air-pump, whereby a temperature as low as −100° C. can be obtained, and large quantities of mercury may easily be frozen.

Carbon dioxide is now liquefied on the large scale, and is employed to a considerable extent in the arts. The chief source of the gas used for this purpose is that given off in the process of fermentation, which in some of the larger breweries is said to amount to many tons a day.

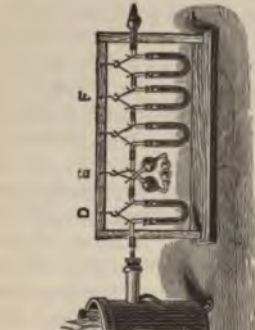

Fig. 29.

The composition of carbon dioxide may be ascertained with great exactness by burning a known weight of pure carbon, such as the diamond or graphite, in a current of pure oxygen gas, and weighing the carbon dioxide produced. The apparatus for the synthesis of this gas is represented in Fig. 29. The weighed quantity of diamond, placed in a small platinum boat, is pushed into the porcelain tube, which can be strongly heated in the furnace. One end of this tube is connected with a gas-holder and drying tubes, A, B, C, by means of which pure and dry oxygen gas is supplied. The other end is connected, as is seen, with a number of tubes and bulbs destined to absorb the carbon dioxide formed by the combustion : the tube D and the bulb E contain a solution of caustic potash, and the other tubes, F, are filled with pumice-stone and sulphuric acid. The bulbs and tubes are carefully weighed, and then the apparatus is filled with pure oxygen, and the tube slowly brought to a red-heat. The gas passes gradually through the system of tubes, and carries along with it the carbon dioxide formed by the combustion of the diamond : the gas is wholly absorbed by the potash in the tube and bulbs, whilst any moisture which might be given off from the bulbs is taken up by the tubes F. The oxygen gas is dried as it enters and also as it leaves the apparatus; so that the gain in weight which the tubes have experienced gives exactly the weight of carbon dioxide formed by the combustion of the carbon of the diamond. Usually the diamond contains a small quantity of ash, or mineral matter, which is incombustible; and this weight must be subtracted from the original weight of the diamond in order that we may know the exact weight of pure carbon burnt: for this reason the diamond is placed in a platinum boat, which can be withdrawn and weighed after the experiment, and the amount of ash thus determined. Another precaution that must be taken is, to fill the greater part of the red-hot tube with porous copper oxide, in case any trace of carbon monoxide (CO) should be formed by the incomplete combustion of the carbon: this gas would pass unabsorbed through the potash unless it be oxidized to carbon dioxide by the heated copper oxide. In this way it has been shown that 100 parts of carbon dioxide consist of

Carbon	27·27
Oxygen	72·73
Carbon Dioxide .	100·00

If we divide 27·27 by the combining weight of carbon and 72·73 by that of oxygen, we have $\frac{27{\cdot}27}{11{\cdot}97} = 2{\cdot}278$ and $\frac{72{\cdot}73}{15{\cdot}96} = 4{\cdot}557$; or the relation between the number of atoms of carbon and that of those of oxygen is that of 1 to 2, so that the formula of carbon dioxide is CO_2. Hence the gas should contain its own volume of oxygen; for 43·89 parts by weight of carbon dioxide, occupying a volume equal to that occupied by 2 parts by weight of hydrogen, contain 31·92 parts by weight of oxygen, which likewise occupy a volume equal to that of 2 parts of hydrogen. That this is the case can be experimentally proved by burning charcoal in a known volume of oxygen in excess, when it is observed that, after the gas has cooled, no alteration in its volume has occurred: hence the volume of carbon dioxide formed must be precisely equal to that of the oxygen used in its formation.

LESSON IX.

Carbon Monoxide, or *Carbonic Oxide Gas.*

Symbol CO, *Molecular Weight* 27·93, *Density* 13·96.—When carbon burns with a limited supply of oxygen, carbonic oxide is formed. The production of this gas in an ordinary red-hot coal fire is often observed; oxygen of the air, which enters at the bottom of the grate, combines with the carbon of the coal, forming carbon dioxide; this substance then passing upwards over the red-hot coals, parts with half its oxygen to the red-hot carbon: thus:

$$CO_2 + C = 2CO.$$

This carbon monoxide on coming out at the top of the fire meets with atmospheric oxygen, with which it at once combines, burning with a lambent blue flame, and re-forming carbon dioxide. Carbon monoxide gas in the pure state can be prepared by passing a slow current of carbon dioxide over pieces of charcoal heated to redness in a tube by means of a furnace, as represented in Fig. 30: it may likewise be obtained in the pure state from several compounds of carbon. Thus, if crystallized oxalic acid be heated with strong sulphuric acid, a mixture of equal volumes of carbon monoxide and carbon dioxide gases is evolved: this latter can be easily separated from the former by shaking the mixed gas up with caustic soda solution, when sodium carbonate will be formed, half the volume of the gas will disappear, and the remainder will be found to be pure carbon monoxide. This decomposition of oxalic acid results from the fact that sulphuric acid has a strong tendency to abstract water, or the elements of water, from the bodies with which it comes into contact: thus the oxalic acid, which may be represented as $C_2H_2O_4$ (see p. 365), being deprived of the elements of one molecule of water, which are taken up by the sulphuric acid, yields a compound, C_2O_3, which cannot exist alone, and immediately splits up into CO_2 and CO.

Carbon monoxide can also be prepared by heating formic acid, CH_2O_2 (see p. 335), with sulphuric acid; here, as with oxalic acid, the elements of water are removed, and pure CO is thus evolved.

Carbon monoxide is a colourless, tasteless gas, which can be condensed to a liquid, the boiling point of which is $-193°$, or about the same as that of nitrogen; it is little lighter than air, its specific gravity being 0·969 (air = 1), and is but very slightly soluble in water. It acts as a strong poison, producing death when inhaled even in very small quantities, the fatal effects often observed of the fumes from burning charcoal or from limekilns being due to the presence of this gas.

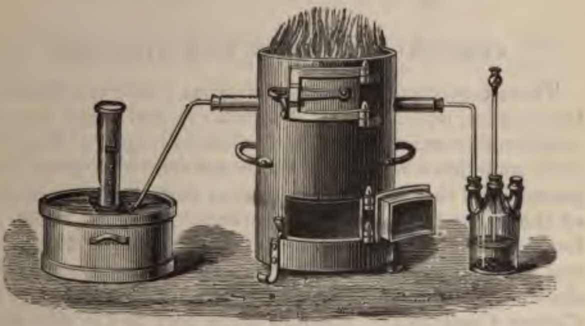

FIG 30.

When heated in contact with oxygen, carbon monoxide takes fire, burning with a characteristic lambent blue flame, and forming carbon dioxide. In contact with caustic potash at a high temperature, carbon monoxide produces potassium formate, thus:

$$KOH + CO = KCHO_2.$$

Caustic potash and carbon monoxide give potassium formate.

Carbon monoxide is absorbed by a solution of cuprous chloride, CuCl, and this serves as a means of separating it from other gases.

The composition of this gas can be ascertained by combustion in the eudiometer with oxygen. 100 volumes of carbon monoxide and 75 volumes of oxygen yield on passing the electric spark 125 volumes, of which 100 are found to be absorbed by caustic potash, and hence are carbon dioxide, the remaining 25 volumes being unaltered oxygen.[1] Hence the volume of carbon dioxide produced is equal to that of the carbon monoxide taken, whilst the volume of oxygen needed is half as large. But as carbon dioxide contains its own volume of oxygen, carbon monoxide must contain half its volume of oxygen; or two volumes of this gas weighing 27·93 contain one volume of oxygen weighing 15·96, and hence 11·97 parts of carbon by weight; therefore its molecular formula is CO.

COMPOUNDS OF CARBON WITH HYDROGEN.

These compounds are very numerous; they are known in the gaseous, liquid, and solid forms. A still larger number of substances exist containing carbon, hydrogen, and oxygen, with sometimes nitrogen; these are termed *organic compounds*, and they are more numerous than all the compounds of the other elements put together. Many of these are found to be produced in the bodies of plants and animals, and their properties are hereafter considered under the division of *Organic Chemistry*, or the *Chemistry of the Carbon Compounds*. We now have only to describe some of the simplest of these compounds.

Methane, *Light Carburetted Hydrogen*, or *Marsh Gas*.

Symbol CH_4, *Molecular Weight* 15·97, *Density* 7·98.—This is a colourless, tasteless, inodorous gas, capable of liquefaction under very great pressure and at very low temperatures. It is found in coal mines, and known under the name of *fire-damp*; it also occurs in stagnant pools, being produced by the decomposition of dead leaves—whence the name marsh gas; it is one of the constituents of coal gas, &c., and is evolved in many volcanic districts. Marsh gas may also be artificially prepared by heating sodium acetate (see p. 338) with caustic soda, thus:

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[1] It is a remarkable fact that if the two gases, oxygen and carbon monoxide, be perfectly dry, the passage of an electric spark fails to bring about combination, whereas if the slightest trace of moisture be present, an explosion at once occurs. The same is true for a mixture of hydrogen and oxygen, and other mixtures of gases.

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

Sodium acetate and caustic soda give sodium carbonate and marsh gas.

It cannot be obtained by the direct union of its elements, but is formed when a mixture of the vapour of carbon disulphide and sulphuretted hydrogen gas is passed over red-hot metallic copper, thus:

$$8Cu + CS_2 + 2H_2S = CH_4 + 4Cu_2S.$$

Marsh gas burns with a bluish-yellow non-luminous flame, forming carbon dioxide and water; with a limited supply of air it yields several products, amongst which is *acetylene*, C_2H_2. If mixed with ten times its volume of air, or twice its volume of oxygen, it ignites on the application of a light, with a violent explosion, and hence the great damage produced by the sudden escape of large volumes of this gas in coal mines. The composition of marsh gas is ascertained by exploding it with oxygen in the eudiometer. One volume of this gas and 3 volumes of oxygen yield 2 volumes after passage of the spark. On absorbing by potash the carbon dioxide produced, 1 volume of oxygen is found to remain. Hence of the 2 volumes of oxygen needed to burn the 1 volume of marsh gas, 1 has gone to unite with the carbon, and 1 to form water with the hydrogen. It is thus seen that 2 volumes of marsh gas contain 4 volumes of hydrogen weighing 4 (as water contains 2 volumes of hydrogen and 1 of oxygen), and as much carbon as is contained in 2 volumes of carbon dioxide, viz. 11·97 parts by weight: and hence the molecular formula CH_4 is given to this gas.

Acetylene, or *Ethine*.

Symbol C_2H_2, *Molecular Weight* 25·94, *Density* 12·97.—This gas is formed by the direct union of carbon and hydrogen at a very high temperature. For this purpose the carbon terminals of a powerful galvanic battery are brought together in an atmosphere of hydrogen. At the high temperature thus evolved, a direct union of carbon and hydrogen takes place, and acetylene is formed. Acetylene is a colourless gas, which burns with a bright luminous flame and possesses a disagreeable and every peculiar odour : it is produced in all cases of incomplete combustion, and its smell may be noticed when a candle burns with a smoky flame. Acetylene combines with certain metals, such as copper and silver, and the compounds thus formed are distinguished by the ease with which they undergo explosive decomposition. This gas likewise unites directly with hydrogen, forming the next substance, ethylene, thus :

$$C_2H_2 + H_2 = C_2H_4.$$

When subjected to a pressure of 22 atmospheres at 0° acetylene is condensed to a colourless mobile liquid lighter than water.

Ethylene, or *Olefiant Gas.*

Symbol C_2H_4, *Molecular Weight* 27·94, *Density* 13·97.—This gas is also obtained on the destructive distillation of coal, and is an important constituent of coal gas. It is obtained in the pure state by heating 1 part of alcohol (spirits of wine), C_2H_6O, with 5 or 6 parts by weight of strong sulphuric acid ; as in the formation of carbon monoxide from formic acid, so in this case the elements of water are separated by the sulphuric acid, and C_2H_4 is evolved as a gas. This gas is colourless, but possesses a sweetish taste ; by exposure to a high pressure at a temperature of $-110°$ it has been condensed to a colourless liquid which does not solidify at $-139°$. Hence liquid ethylene remaining transparent during its volatilization has an advantage over liquid carbon dioxide or liquid nitrous oxide, and is now employed as a means of condensing the other less easily liquefiable gases. On bringing this gas in contact with a flame in the air, it burns with a luminous smoky flame forming carbon dioxide and water. When mixed with three times its bulk of oxygen and fired, it detonates very powerfully. One volume of olefiant gas requires 3 volumes of oxygen to burn it completely, and yields 2 volumes of carbon dioxide ; so that 1 volume of oxygen is needed to combine with the hydrogen. Hence this gas contains twice as much carbon as marsh gas with the same quantity of hydrogen ; we must therefore write its molecular formula C_2H_4.

Olefiant gas combines directly with its own volume of chlorine gas, forming an oily liquid, $C_2H_4Cl_2$; and owing to this property the gas has received the above name.

COAL GAS.

The gas so largely used for illuminating purposes, and obtained by the destructive distillation of coal (*i.e.* by heating the coal in large closed retorts so as to decompose or destroy the coal, the volatile products of this decomposition being condensed and collected,) is not a simple chemical compound, but a mixture of varying quantities of a large number of distinct substances. In order to prepare coal gas of good quality, cannel or some highly bitumenized coal is heated in a closed retort : volatile bodies are thus formed and expelled, whilst a residue of (impure) carbon is left behind as coke. The volatile products of this decomposition may be distinguished as tar, ammonia-water, and gas. The tar contains a great variety of substances, from some of which the well-known aniline colours are produced (see *Org. Chem.*) ; and the ammonia derived from the nitrogen in the coal is our chief source of ammoniacal salts (see p. 71). The gas which comes off consists of a mixture of various substances, some of which are useful for illuminating or heating purposes, whilst some are hurtful and must be removed. Amongst those which burn with a luminous flame are olefiant gas and other hydrocarbons, of which propylene, C_3H_6, and benzene vapour, C_6H_6, are the most important. The gases which serve to dilute these luminous hydrocarbons, and which burn themselves with non-luminous flames, are hydrogen, carbonic oxide, and marsh gas. The impurities consist of carbon dioxide, hydrogen sulphide (sulphuretted hydrogen), and the vapour of carbon disulphide ; and these substances are almost always completely withdrawn from the gas by a system of purification before it is sent out from the gasworks. The relative proportion of the ingredients present in coal gas varies greatly according to the kind of coal employed, and according to the heat to which the coal is subjected. This is seen from the following table, in which the composition of a gas made from common coal, together with that of one made from cannel-coal, is given.

	Illuminating power; in Candles per 5 cubic feet.	COMPOSITION IN 100 VOLUMES.					
		Hydrogen, H.	Marsh Gas, CH_4.	Heavy Hydrocarbons, C_nH_{2n}.	Equal to Olefiant Gas, C_2H_4.	Carbonic Oxide, CO.	Nitrogen, Oxygen, and Carbonic Acid.
Cannel gas	34·4	25·82	51·20	13·06	(22·08)	7·85	2·07
Coal gas . .	13·0	47·60	41·53	3·05	(6·97)	7·82	—

The value of coal gas, as regards its illuminating power, is ascertained by comparing the light given off by the gas burning at a certain rate, usually 5 cubic feet per hour, with that of a sperm candle burning 120 grains per hour. Thus the cannel gas is said to be equal to 34·4 candles, and the coal gas to be equal to 13 candles.

Another kind of gas now largely used, especially in the United States, is known as *water-gas*, and is prepared by passing steam over red-hot coke:

$$C + H_2O = CO + H_2.$$

It consists chiefly of hydrogen and carbon monoxide, together with some carbon dioxide, and burns with a pale, non-luminous, very hot flame, and is therefore employed largely for steel-melting, &c. To use it as an illuminating agent, a comb of magnesia or other refractory substance is introduced into the flame, being thus intensely heated and emitting a powerful light.

STRUCTURE OF FLAME.

It will be convenient here to mention the nature and structure of flame, and the principle of the Davy lamp. Flame consists of gas in a high state of ignition. When a jet of burning hydrogen is plunged into oxygen, the flame of *hydrogen in oxygen* is seen. This is caused by the ignition of the particles of hydrogen and oxygen, owing to the heat evolved in their combination. A similar flame of *oxygen in hydrogen* is seen when a jet of the former gas is lit in an atmosphere of hydrogen. The temperatures of flames differ as much as their illuminating powers, and the hottest flames do not necessarily give off much light : thus the oxyhydrogen flame, which is so hot as to burn iron or steel wire like tinder, can scarcely be seen in bright daylight. In order that a flame shall give off much light, it must contain solid matter, which becomes heated up to whiteness. If a piece of lime be held in the oxyhydrogen flame, it becomes strongly heated, and gives off an intense light : so also if we bring solid matter, such as powdered charcoal, into the colourless flame of hydrogen, it becomes luminous. The difference between the non-luminous flame of marsh gas and the luminous flame of olefiant gas is due to the fact, that in the latter carbon is separated out in the solid form, whereas in the former all the carbon is at once burnt to carbonic acid. The flame of a candle consists of three distinct parts—(1), the dark central zone or supply of unburnt gas surrounding the wick ; (2), the luminous zone or area of incomplete combustion ; and (3), the non-luminous zone or area of complete combustion. If we bring one end of a small bent piece of glass tubing (Fig. 31) into the dark central zone (1), the unburnt gases will pass up the tube, and may be ignited at the other end, where they escape into the air. In the luminous part of the flame the gases are not completely burnt, and carbon is separated out in the solid state ; and it is to the presence of this carbon that the flame owes its luminous power. In the outer zone the supply of oxygen is greater, all the carbon is at once burnt to carbon dioxide, and the flame here becomes non-luminous.[1]

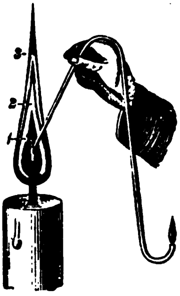

FIG. 31.

The effect of allowing a complete combustion to proceed at once throughout the flame is well seen in the small Bunsen gas-lamp, now universally employed in laboratories. In this lamp (Fig. 32) the coal gas issues from a small central burner (*a*), and passing unburnt up the tube (*e*) draws air up with it through the holes (*d*); the mixture of air and gas thus made can be lighted at the top of the tube, where it burns with a non-luminous, perfectly smokeless flame: if the holes (*d*) be closed, the gas alone burns with the ordinary bright smoky flame. The blowpipe flame (Fig. 33) may also be divided into two distinct parts—the oxidizing flame (*a*), where there is excess of oxygen, and the reducing flame (*b*), where there is excess of carbon; and these are distinguished by the same properties as the outer and inner mantle of the candle flame. Every mixture of gases requires a certain temperature to inflame it; and if this temperature be not reached, the mixture does not take fire; we may thus cool down a flame so much that it goes out, by placing over it a small coil of cold copper wire: whereas, if the coil be previously heated, the flame will continue to burn. The same fact is well shown with a piece of wire gauze containing about 700 meshes to the square inch: if this be held close over a jet of gas, and the gas lit, it is possible to remove the gauze several inches above the jet, and yet the inflammable gas below does not take fire, the flame burning only above the gauze (Fig. 34). The metallic wires in this case so quickly conduct away the heat that the temperature of the gas at the lower side of the gauze cannot rise to the point of ignition. This simple principle was made

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[1] The optical difference between these two classes of flame is pointed out in the paragraph on Spectrum Analysis (see p. 266).

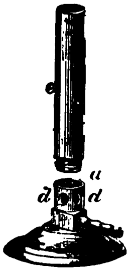

FIG. 32.

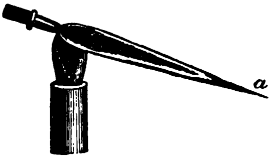

FIG. 33.

use of by Sir Humphry Davy in his safety-lamp for coal mines. It consists of an oil lamp (Fig. 35), the top of which is inclosed in a covering of wire gauze; the air can enter through the meshes of the gauze, and the products of combustion of the oil can escape, but no flame can pass from the inside to the outside of the gauze; and hence, even if the lamp be placed in a most inflammable mixture of fire-damp and air, no ignition is possible, although the combustible gas may take fire and burn inside the gauze. It is, however, then advisable that the miner should withdraw, to avoid risk of explosion of the gas from the gauze thus becoming overheated and inflaming the fire-damp which surrounds it.

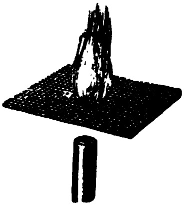

FIG. 34.

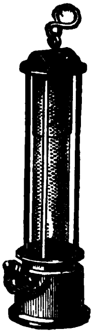

FIG. 35.

The compounds of carbon being generally of a more complicated nature than the preceding ones, will be more completely considered under the head of Organic Chemistry.

CARBON AND NITROGEN.

Cyanogen Compounds.—Carbon and nitrogen do not unite together directly, but if nitrogen gas be passed over a white-hot mixture of charcoal and potassium carbonate, a remarkable compound termed potassium cyanide, KCN, is formed, thus:

$$K_2CO_3 + N_2 + 4C = 2KCN + 3CO.$$

From this substance a large number of bodies can be prepared, all of which contain the group of atoms CN, and possess characteristic and peculiar properties : to this group the name Cyanogen is given, from its forming a number of blue compounds (κύανος blue, and γεννάω I produce). Cyanogen combines with metals to form *cyanides*, and in this respect resembles chlorine ; and it belongs to a class of bodies termed *compound radicals*, of which we shall have to speak hereafter.

Cyanogen compounds are prepared on a large scale for various purposes by heating nitrogenous organic matter, such as clippings of hides, hoofs, &c., with iron and potashes ; a double cyanide containing iron and potassium, called potassium ferrocyanide, or yellow prussiate of potash (see Organic Chemistry, p. 303) is formed.

The most important compound formed by cyanogen is one with hydrogen (analogous in composition to hydrochloric acid, HCl), and called *hydrocyanic acid*, or commonly *prussic acid*, HCN. This substance is prepared by acting on potassium cyanide with dilute sulphuric acid in a retort. Hydrocyanic acid mixed with water distils over, leaving potassium sulphate in the retort.

If the aqueous distillate be shaken up with mercuric oxide, the hydrogen of the hydrocyanic acid is replaced by mercury, and mercuric cyanide, $Hg\,(CN)_2$, is formed, which may be obtained by evaporation in the form of white crystals.

Hydrocyanic acid is prepared pure and free from water by passing sulphuretted hydrogen gas, H_2S, over dry mercuric cyanide, hydrocyanic acid and mercuric sulphide being formed, thus :

$$Hg(CN)_2 + H_2S = 2HCN + HgS.$$

Mercuric cyanide and sulphuretted hydrogen yield hydrocyanic acid and mercuric sulphide.

Hydrocyanic acid thus prepared is a volatile liquid, boiling at $26^{\circ}\cdot5$, and solidifying at -15° ; it is one of the most poisonous substances known, a single drop of the pure acid being sufficient to produce fatal results : much care must therefore be taken in its preparation not to inhale the vapour, which, even in small quantity, may produce death. It possesses a peculiar and characteristic smell of bitter almonds, and occurs in small quantities in the kernels and leaves of many plants.

Cyanogen Gas, or *Dicyanogen*, $\left.\begin{matrix}CN\\CN\end{matrix}\right\}$, can be easily obtained as a colourless gas by heating mercuric cyanide. It is best collected over mercury, as it is soluble in water. It condenses to a colourless liquid when exposed to a pressure of about four atmospheres; it is inflammable, and burns with a beautiful purple flame, forming carbon dioxide, CO_2, and free nitrogen.

Cyanogen forms a large number of compounds, some of them of a very complicated constitution and connected with other carbon compounds, together with which they will be considered.

LESSON X.

We now pass to the consideration of a group of elements which resemble each other closely, and possess strongly-marked and active properties: viz. *Chlorine*, *Bromine*, *Iodine* and *Fluorine*.

CHLORINE.

Symbol Cl, *Atomic Weight* 35·37, *Density* 35·37.—Chlorine was discovered in the year 1774 by Scheele; it does not occur free in nature, but can easily be prepared from its compounds. It is found combined with metals forming chlorides; of these sodium chloride, sea- or rock-salt, is the most common: to obtain chlorine from this, it must be heated with sulphuric acid and manganese dioxide, thus:

$$4NaCl + 3H_2SO_4 + MnO_2 = Cl_2 + 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O.$$

If 11 parts by weight of salt to 5 parts of manganese dioxide be mixed with 14 parts of sulphuric acid diluted with an equal volume of water, and the mixture brought into a large flask, the chlorine gas is given off regularly upon the application of a very slight heat: in order to obtain the gas pure, it may be passed through the water contained in a wash-bottle before it is collected for use. Chlorine may also be readily prepared from granulated manganese dioxide and hydrochloric acid. The following reaction first takes place:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

On heating the manganese tetrachloride it splits up into manganese dichloride and chlorine:

$$MnCl_4 = MnCl_2 + Cl_2.$$

Chlorine is a greenish-yellow gas, whence its name (χλωρός), possessing a most disagreeable and peculiar smell, which, when the gas is present in small traces only, resembles that of seaweed, but when present in large quantities acts as a violent irritant, producing inflammation of the mucous membrane, and even causing death when inhaled. Chlorine gas when submitted to a pressure of six atmospheres at the ordinary temperature is condensed to a heavy yellow liquid, and this solidifies at $-102°$ to a yellow crystalline mass. This gas cannot be collected over water or mercury, as it is soluble in the former (1 volume of water dissolving 2·37 volumes of chlorine at 15°), and combines directly with the latter forming mercuric chloride. It can, however, be easily collected by downward displacement, as it is 2·45 times as heavy as air. Many elements in a finely divided state when brought into chlorine gas, take fire spontaneously, forming metallic chlorides; thus phosphorus, powdered arsenic, antimony, or thin copper leaf, burn when thrown into the gas. The density of chlorine remains constant when the gas is heated to 1300°.

Chlorine is not combustible, and its most remarkable property is its power of combining with hydrogen to form hydrochloric acid: when equal volumes of these two gases are mixed together, they combine with explosion on bringing a flame into contact with them, or on exposing the mixture to sunlight. Chlorine is even able to decompose water in the sunlight, combining with the hydrogen and liberating the oxygen. Several experiments illustrative of this property of chlorine may be mentioned. If a burning candle be plunged into this gas, the taper continues to burn, but with a very smoky flame, the hydrogen of the wax alone entering into combination with the chlorine, whilst the carbon is given off as smoke or soot: the same effect is produced when a paper moistened with turpentine (a compound of carbon and hydrogen) is held in a jar of chlorine gas; the hydrogen of the turpentine at once combines with the chlorine, forming hydrochloric acid, and the carbon is liberated; so much heat is given off by this action that the turpentine frequently takes fire.

The well-known bleaching action of chlorine also depends upon its power of combining with the hydrogen of water and liberating the oxygen:

$$Cl_2 + H_2O = 2HCl + O.$$

Dry chlorine gas does not bleach; we may inclose a piece of cotton cloth or paper coloured by a vegetable substance, such as madder or indigo, in a bottle of dry chlorine, and no change of colour takes place, even after the lapse of many weeks: if, however, a few drops of water be added, the colouring matter is immediately destroyed, and the cotton or paper is bleached. Here the chlorine combines with the hydrogen of the water, and the oxygen at the moment of its liberation (when it is said to be *nascent*) combines with the vegetable colouring matters, forming compounds destitute of colour. Ordinary free oxygen has not this power—not at least to any great extent; and it is a frequent observation that bodies in this *nascent state* have more active properties than the same bodies when in the free state. This difference depends upon the fact that the *molecules*, or smallest particles of an element which can exist in the free state, do not consist of the individual atoms, but of groups of atoms. The molecule of a compound body contains two or more dissimilar atoms, whilst that of an element contains similar atoms. *Equal volumes of all bodies simple or compound, in the gaseous state, contain the same number of molecules.* Thus, free oxygen is $\left\{\begin{matrix} O \\ O \end{matrix}\right.$; free hydrogen $\left\{\begin{matrix} H \\ H \end{matrix}\right.$; free chlorine $\left\{\begin{matrix} Cl \\ Cl \end{matrix}\right.$: similarly, free cyanogen is $\left\{\begin{matrix} CN \\ CN \end{matrix}\right.$. Now, the moment an element is liberated from a compound, the single atoms unite together to form a molecule, and the elementary body makes its appearance in the free state: if, however, substances are present on which the element can act chemically, they are decomposed by the chemical attractions of the liberated atoms, these being more active in that state than when united to form a molecule.

Although, as above stated, chlorine acts upon water with formation of hydrochloric acid and oxygen, the reverse reaction may be made to take place under certain conditions. Thus when hydrochloric acid gas is mixed with oxygen or air and passed over bricks saturated with copper sulphate, large quantities of chlorine are formed, and the gas is now prepared on the large scale by this means, the method being known as "Deacon's process." The copper sulphate undergoes no change, and acts for an indefinite length of time.

Chlorine is unable to bleach mineral colours: the difference between printer's ink, coloured by lampblack or carbon, and writing ink, a vegetable black, is well illustrated by placing a sheet of paper having characters written and printed upon it in a solution of chlorine in water.

Chlorine gas is largely used for bleaching purposes in the cotton, linen, and paper manufactures. It is sometimes used in the form of a gas, but more usually in combination with calcium and oxygen, forming the article called chloride of lime, or bleaching powder (p. 105). Chlorine is also largely employed as a disinfectant and deodorant, its action on organic putrefactive substances being similar to that upon organic colouring matters.

CHLORINE AND HYDROGEN.

Hydrochloric Acid, or Hydrogen Chloride.

Symbol HCl, *Molecular Weight* 36·37, *Density* 18·18.—This substance, the only known compound of chlorine and hydrogen, is obtained when equal volumes of chlorine and hydrogen are mixed and exposed to the diffused light of day; the gases then combine, and form an equal volume of hydrochloric acid gas. If the light be strong, this combination takes place so rapidly that a violent explosion occurs, owing to the sudden disengagement of heat consequent upon the combination. The volume of hydrochloric acid formed is, as already stated, equal to that of the chlorine and hydrogen; one molecule of hydrogen and one molecule of chlorine gives two molecules of hydrochloric acid, thus:

$$\left.\begin{matrix}H\\H\end{matrix}\right\} + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\} = \left.\begin{matrix}H\\Cl\end{matrix}\right\} + \left.\begin{matrix}H\\Cl\end{matrix}\right\}.$$

Hydrochloric acid is, however, usually prepared by heating common salt (sodium chloride) and sulphuric acid in a flask, as seen in Fig. 36. The gas is first purified by passing through a wash-bottle containing a little water, and then is either collected by displacement (if the gas is required) or passed into water (as represented in the figure) if an aqueous solution of the acid is needed.

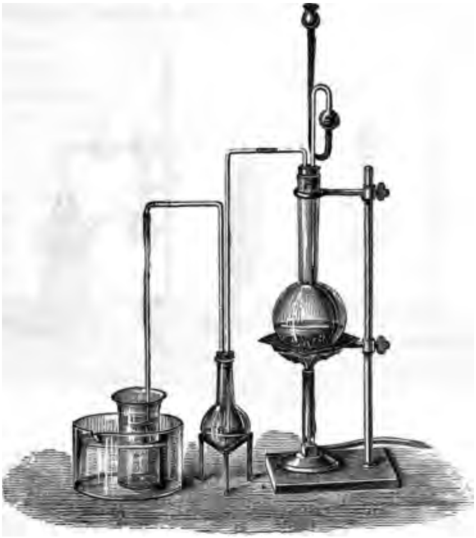

FIG. 36.

$$NaCl + H_2SO_4 = HCl + NaHSO_4.$$

Sodium chloride and sulphuric acid give hydrochloric acid and hydrogen sodium sulphate.

Hydrochloric acid is a colourless gas, 1·269 times heavier than air; it fumes strongly in damp air, combining with the moisture, and has a strongly acid reaction. It is very soluble in water, one volume of this liquid at 15° dissolving 454 volumes of the gas: this colourless or yellowish solution is the ordinary hydrochloric or muriatic acid of the shops. Under a pressure of 40 atmospheres the gas forms a limpid liquid which solidifies when cooled to −116°. The gas can be collected over mercury, and its solubility in water strikingly shown by allowing a few drops of water to ascend to the surface of the mercury in contact with the gas: a rapid rise of the mercury in the jar immediately occurs. A saturated solution of hydrochloric acid in water has the specific gravity of 1·21; it fumes strongly in the air, and, when heated in a retort, loses at first hydrochloric acid gas, but after a time an aqueous acid distils over at ordinary atmospheric pressure, containing 20·22 per cent. of HCl, and boiling constantly at 110°. If the distillation be conducted under a diminished pressure, the acid boils constantly at a lower temperature, and attains a composition which is different for each boiling point; hence the constant acids thus obtained by boiling the solution of hydrochloric acid gas in water cannot be considered as definite compounds of HCl and water. This fact holds good for many other aqueous solutions of acids, &c.; viz. that residues constantly boiling at the same temperature,

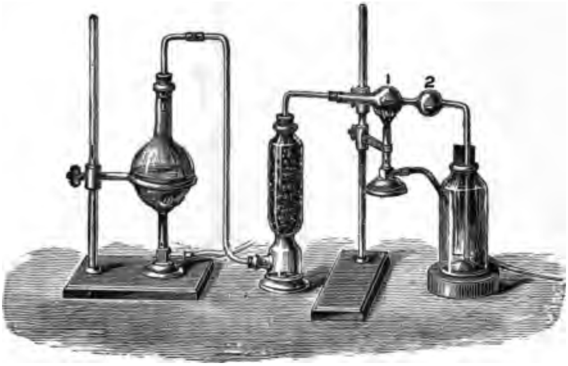

FIG. 37.

and having constant compositions, are obtained on distillation, the composition and boiling point varying however, with the pressure under which the distillation has been conducted.

Enormous quantities of hydrogen chloride (commonly called muriatic acid, from *muria* brine) are obtained as a by-product in the manufacture of sodium carbonate (see p. 194). More than 1,000 tons of this acid are made every week in the South Lancashire district alone. The acid thus produced is, however, not pure, having a yellow colour, and containing in small quantities iron, arsenic, organic matter, and sulphuric acid in solution.

Composition of Hydrochloric Acid.—The arrangement represented in Fig. 37 is adapted to show that, when gaseous hydrochloric acid is passed over heated manganese dioxide, water and chlorine gas are formed, thus :

$$4HCl + MnO_2 = Cl_2 + 2H_2O + MnCl_2.$$

If the gas is allowed to pass over the oxide contained in the first bulb before it is heated, no formation of water is noticed, and the red litmus-paper in the bottle remains coloured ; as soon as the oxide is heated, moisture is at once seen to be deposited in the second bulb, and the paper becomes bleached, showing the presence of chlorine.

The exact composition of hydrogen chloride is best determined by decomposing the aqueous acid in the dark by means of a current of voltaic electricity, by an arrangement similar to that shown in Fig. 13, but in which the platinum electrodes are replaced by carbon ; the gases (hydrogen and chlorine) evolved are collected in a long tube, after allowing the decomposition to go on for some time. If the tube thus filled be opened in the dark under a solution of potassium iodide, the solution will rise in the tube, the iodine being liberated, the chlorine combining with the potassium, until exactly half the tube is filled with liquid ; the remaining gas is found to consist of hydrogen. If the mixture of electrolytic gases, which can with care be sealed up in a strong tube having very finely drawn-out ends, be exposed to the action of daylight, or of a bright artificial light, such as that of burning magnesium wire, immediate combination of the two gases will ensue, and on opening one of the ends under water this liquid will completely fill the whole of the tube, showing that the component gases were present in exactly the proportion needed to form hydrochloric acid gas, which dissolves in the water.

Tests for Hydrochloric Acid.—The presence of hydrochloric acid is detected by the fact that it gives a white precipitate with silver nitrate, soluble in ammonia but insoluble in nitric acid, and by the fact that on heating with manganese dioxide and sulphuric acid it gives off chlorine, recognized by its bleaching action and unpleasant smell.

Nitro-hydrochloric Acid, or *Aqua Regia.*

Certain metals, such as gold and platinum, and many metallic compounds, such as certain sulphides, which do not dissolve in either nitric or hydrochloric acid separately, are readily soluble in a mixture of both of these acids, especially upon warming. This mixture has been termed *aqua regia* (because it dissolves gold, *rex metallorum*); its solvent action depends upon the fact that it contains free chlorine, liberated by the oxidizing action of nitric acid on the hydrogen of the hydrochloric acid. The metals combine directly with this free chlorine to form soluble chlorides, and the sulphides are decomposed by it. The nitric acid is reduced to nitrogen dioxide, and this combines with a portion of the chlorine to form the compound $NOCl$, which is liberated as a yellowish gas, condensing to a dark yellow, very volatile liquid when it is led into a freezing mixture. The same compound is formed by direct combination when the two gases, nitrogen dioxide and chlorine, are mixed together.

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine and oxygen do not unite directly, but they may indirectly be made to form two oxides, viz. chlorine monoxide, Cl_2O, and chlorine peroxide, ClO_2,[1] whilst chlorine, oxygen and hydrogen unite in four proportions, giving rise to the following *oxyacids of chlorine* :

---

[1] An oxide of the formula Cl_2O_3 was formerly supposed to exist, but has recently been shown to consist of a mixture of the other two.

Hypochlorous Acid, or *Hydrogen Hypochlorite*, $HClO$.
Chlorous Acid, or *Hydrogen Chlorite*, $HClO_2$.
Chloric Acid, or *Hydrogen Chlorate*, $HClO_3$,
Perchloric Acid, or *Hydrogen Perchlorate*, $HClO_4$.

Chlorine Monoxide.

Symbol Cl_2O, *Molecular Weight* 86·7, *Density* 43·35.—Chlorine monoxide is obtained by the action of chlorine upon mercuric oxide—the chlorine combining not only with the metal, but also with the oxygen, thus:

$$HgO + 2Cl_2 = Cl_2O + HgCl_2.$$

Mercuric oxide and chlorine give chlorine monoxide and mercuric chloride.

It is a yellowish gas, which may be condensed by means of a freezing mixture to a red liquid, which is very explosive, decomposing very suddenly into chlorine and oxygen gases.

It is very soluble in water, yielding a yellow solution, which bleaches powerfully, and destroys vegetable colouring matter more rapidly than chlorine, inasmuch as twice as much oxygen is liberated from one molecule of chlorine monoxide as from one molecule of chlorine, thus:

$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\} + \left.\begin{matrix}H\\H\end{matrix}\right\} O = 2\left.\begin{matrix}H\\Cl\end{matrix}\right\} + O.$$

$$\left.\begin{matrix}Cl\\Cl\end{matrix}\right\} O + \left.\begin{matrix}H\\H\end{matrix}\right\} O = 2\left.\begin{matrix}H\\Cl\end{matrix}\right\} + O_2.$$

If a current of chlorine gas be led into a dilute and cold solution of caustic soda, a mixture is formed of sodium chloride and a compound having the formula $NaClO$, known as sodium hypochlorite, thus:

$$2NaHO + Cl_2 = NaClO + NaCl + H_2O.$$

Bleaching-Powder.—If slaked lime is employed instead of caustic soda, the chlorine is rapidly absorbed, and the substance well known as bleaching powder (or chloride of lime) is formed.

Bleaching-powder is a compound which on treatment with water forms a mixture of calcium hypochlorite and calcium chloride: it is used in enormous quantities for bleaching purposes, and is prepared on the large scale by passing chlorine gas, generated from manganese dioxide and hydrochloric acid in large stone tanks, or by Deacon's process (p. 100) into spacious chambers, on the floors of which a layer of slaked lime two inches thick is laid : the gas is all absorbed, and bleaching-powder formed. The reaction may be thus explained:

$$2CaH_2O_2 + 2Cl_2 = 2H_2O + CaCl_2 + CaCl_2O_2.$$

Slaked lime and chlorine give water, calcium chloride and calcium hypochlorite.

Hypochlorous Acid, or *Hydrogen Hypochlorite.*

Symbol $HClO$. If a solution of a hypochlorite be mixed with dilute nitric acid and distilled, a solution of hypochlorous acid comes over. It is a colourless liquid, possessing a peculiar smell and powerful bleaching properties.

$$NaOCl + HNO_3 = NaNO_3 + HClO.$$

Sodium hypochlorite and nitric acid give sodium nitrate and hypochlorous acid.

Hypochlorous acid stands therefore in the same relation to chlorine monoxide as nitric acid to nitrogen pentoxide, or as carbonic acid to carbon dioxide. Hydrochloric acid decomposes hypochlorous acid with the evolution of chlorine, thus :

$$\left.\begin{matrix}H\\Cl\end{matrix}\right\}O + \left.\begin{matrix}H\\Cl\end{matrix}\right\} = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}.$$

Hence neither this acid nor sulphuric acid, which liberates hydrochloric acid from the calcium chloride, can be used for the preparation of hypochlorous acid from the hypochlorite ; but they are employed in the process of bleaching for the decomposition of the bleaching-powder, to liberate the chlorine in the fibre of the cloth. This is accomplished by first dipping the goods to be bleached in a solution of bleaching-powder, and then passing them through dilute hydrochloric or sulphuric acid, whereby the chlorine is liberated in the fibre of the cloth : hence the bleaching effect is only visible after the goods have been " soured," or dipped in the acid.

Chlorine Peroxide,

Symbol ClO_2, is a dark yellow gas obtained by the action of sulphuric acid on potassium chlorate. It condenses to a red brown liquid, and is a very dangerous substance, as it is liable to sudden decomposition, producing the most violent explosions. It is soluble in water; the solution does not, however, yield any peculiar salt on treatment with an alkali, but gives mixtures of chlorite and chlorate.

Chlorous Acid, or *Hydrogen Chlorite.*

Symbol $HClO_2$. This acid is not known in the free state, but its salts, termed *Chlorites*, have been obtained.

Chloric Acid, or *Hydrogen Chlorate.*

Symbol $HClO_3$. If excess of chlorine be passed into a warm and concentrated solution of caustic potash, potassium chlorate and potassium chloride are formed, thus:

$$3Cl_2 + 6KHO = KClO_3 + 5KCl + 3H_2O.$$

The potassium chlorate can be easily separated from the more soluble chloride by crystallization. Chloric acid itself can be prepared by decomposing potassium chlorate with hydrofluosilicic acid, whereby an insoluble potassium compound is precipitated, and chloric acid remains in solution; or, by adding sulphuric acid to barium chlorate, insoluble barium sulphate being precipitated, thus:

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

Chloric acid solution may be concentrated in a vacuum over sulphuric acid to a syrup, but it decomposes on further evaporation; it acts as a powerful oxidizing agent, parting with its oxygen, and when dropped upon paper produces ignition.

The chlorates yield up all their oxygen on heating, and the potassium salt is used as a most convenient source of this gas. The composition of chloric acid is ascertained by determining the weight of oxygen, which potassium chlorate yields on heating (see p. 14), together with the amount of chlorine contained in the residual potassium chloride.

Perchloric Acid, or *Hydrogen Perchlorate.*

Symbol $HClO_4$.—When potassium chlorate is heated, it first fuses and begins to give off oxygen : at a certain point, however, the whole mass solidifies ; if the decomposition be stopped at this stage, a new salt will be found to be contained in the residue, together with chloride and unaltered chlorate, thus :

$$2KClO_3 = KClO_4 + KCl + O_2.$$

This new salt is termed Potassium perchlorate, and its composition is $KClO_4$. It may be easily separated from the chlorate by treatment with hydrochloric acid, which decomposes this latter, but has no action on the perchlorate. Perchloric acid, $HClO_4$, can readily be prepared from the potassium salt by the action of strong sulphuric acid. If a mixture of one part of the dry perchlorate and four of sulphuric acid be distilled in a retort, a colourless fuming liquid condenses in the receiver: this is perchloric acid, $HClO_4$. It has a specific gravity of 1·78 at 15°·5, and does not solidify at $-35°$. Perchloric acid is one of the most powerful oxidizing agents known ; when thrown upon wood or paper it produces instant ignition, and when dropped on to charcoal it decomposes with a loud explosion. It combines with water to form a crystalline hydrate, $HClO_4+H_2O$, which when further diluted with water forms a thick oily liquid boiling constantly at 203°, and containing 72·3 per cent. of $HClO_4$, and thus not corresponding to any definite hydrate. This hydrate can also be obtained by boiling a solution of chloric acid, thus :

$$3HClO_3 = HClO_4 + H_2O + Cl_2 + O_4.$$

Perchloric acid is by far the most stable of the acids derived from chlorine.

The acids of chlorine form, as seen, an unbroken series, each member differing from the next by one atom of oxygen :

HCl Hydrochloric acid.
$HClO$, Hypochlorous acid.
$HClO_2$, Chlorous acid.
$HClO_3$, Chloric acid.
$HClO_4$, Perchloric acid.

COMPOUND OF CHLORINE AND NITROGEN.

Chlorine combines with nitrogen, though only indirectly, to form a very remarkable compound, which has the composition NCl_3. If chlorine gas be passed into a solution of ammonia, nitrogen, as we have seen, is liberated; if an excess of chlorine be employed, drops of an oily liquid form, which, on being touched, explode with fearful violence, so that the greatest caution must be used in manipulating even traces of this body. The explosive nature of this compound arises from the fact that its constituent elements are feebly combined, and separate into the elementary gases with sudden violence.

COMPOUNDS OF CHLORINE AND CARBON.

Chlorine and carbon cannot be made to unite directly with one another, but by indirect means four distinct compounds containing these elements can be obtained. One of the most important reactions by which the carbon chlorides can be prepared is by the action of chlorine on certain hydrocarbons, in which the hydrogen can be replaced, atom for atom, by chlorine. Thus with marsh gas the following four stages in this substitution of hydrogen by chlorine occur, the formation of carbon tetrachloride being the last one.

$$
\begin{array}{lllll}
(1)\ CH_4 & + Cl_2 & = CH_3Cl & + HCl. \\
(2)\ CH_3Cl & + Cl_2 & = CH_2Cl_2 & + HCl. \\
(3)\ CH_2Cl_2 & + Cl_2 & = CHCl_3 & + HCl. \\
(4)\ CHCl_3 & + Cl_2 & = CCl_4 & + HCl.
\end{array}
$$

The properties of these and the other carbon chlorides will be discussed under the division of Organic Chemistry.

LESSON XI.

BROMINE.

Symbol Br, *Atomic Weight* 79·75, *Density* 79·75.—This element, which closely resembles chlorine in its properties and compounds, was discovered by Balard, in 1826, in the salts obtained by the evaporation of sea-water. It does not occur free in nature, and is, like chlorine, found combined with soda and magnesium in the waters of certain mineral springs. It is now chiefly prepared from the mother-liquors obtained in the potash industry at Stassfurt, which contain considerable quantities of bromine. In order to prepare it use is made of the fact that free chlorine liberates bromine from its combinations with metals, forming a metallic chloride. The bromine thus set free may be separated by shaking the liquid up with ether, which dissolves the bromine, forming a bright red solution. On adding caustic potash to this ethereal solution, the colour at once disappears, the bromine becomes combined, forming the bromide and bromate of potassium: on evaporation of the ether these salts remain, and after ignition (to decompose the bromate) the bromide can again be liberated by the action of sulphuric acid and manganese dioxide exactly as in the case of chlorine, thus:

$$2BrK + 2H_2SO_4 + MnO_2 = 2Br + K_2SO_4 + MnSO_4 + 2H_2O.$$

Bromine is a dark, reddish-black, heavy liquid (the only element liquid at ordinary temperatures besides mercury); its specific gravity at 0° is 3·188, it freezes at $-7°$ to a black solid, and boils at 59° It possesses a very strong irritating smell, resembling that of chlorine (βρῶμος, a stink), and when inhaled, acts as a strong poison: one part of bromine dissolves in about 30 parts of water at 15°; and this solution possesses bleaching powers, feebler, however, than those of chlorine. This bleaching action is caused by the oxidation of the colouring matter, the bromine combining with the hydrogen of the water to form an acid called hydrobromic acid, corresponding in mode of formation and properties to hydrochloric acid.

The vapour density of bromine has been found to diminish at a high temperature, viz. from 5·52 to 4·4 (air = 1). Hence it appears that a certain number of molecules Br_2 are dissociated into single atoms, Br.

Hydrobromic Acid, or *Hydrogen Bromide*.

Symbol HBr, *Molecular Weight* 80·75, *Density* 40·37.— Hydrogen and bromine do not unite together, even when placed in the sunlight, but they combine to form hydrobromic acid when passed through a red-hot porcelain tube containing metallic platinum. Hydrobromic acid is prepared by the action of acids (phosphoric acid) on the bromides, or better by bringing bromine and phosphorus in contact with water, when a violent action occurs, hydrobromic acid and phosphoric acid being formed, thus:

$$P + 5Br + 4H_2O = 5HBr + H_3PO_4.$$

It is a colourless gas, having a strong acid reaction, and fumes strongly in moist air: it is very soluble in water. When concentrated the aqueous acid boils (under 760 mm. pressure) at 126°, and contains 47·8 per cent. of HBr. Two volumes of this gas contain one of bromine united with one of hydrogen. The aqueous acid neutralizes bases, forming the bromides and water. The gas liquefies at $-73°$.

Tests for Hydrobromic Acid. The presence of the acid is detected by its giving a yellowish white precipitate with silver nitrate which is sparingly soluble in ammonia, readily in potassium cyanide solution; also by its giving off reddish brown vapours of bromine when heated with manganese dioxide and sulphuric acid.

Oxy-acids of Bromine.

No oxides of bromine are known; the oxy-acids are Hypobromous acid, $HBrO$, and Bromic acid, $HBrO_3$.

Hypobromous Acid, $HBrO$, is known only in aqueous solution. It is obtained by the action of bromine water upon mercuric oxide, thus:

$$HgO + 2Br_2 + H_2O = 2HBrO + HgBr_2.$$

Like hydrochlorous acid, it bleaches vegetable colouring matters by oxidation, hydrobromic acid being formed. Bromine gives with slaked lime a compound analogous to bleaching-powder, which with water yields a solution consisting of a mixture of calcium bromide and calcium hypobromite.

Bromic Acid, $HBrO_3$, can be obtained by the action of chlorine upon bromine water, thus:

$$Br + 3H_2O + 5Cl = 5HCl + HBrO_3.$$

In both its properties and composition it corresponds to chloric acid. Certain metallic bromates can be obtained, like the corresponding chlorates, by the action of bromine on the metallic oxides in aqueous solution. The best method of obtaining the bromates of the alkali-metals (potassium and sodium) consists in saturating a concentrated solution of the metallic carbonate with chlorine until carbonic acid begins to escape, and then adding bromine; all the chlorine is liberated, and solution of pure bromate remains. Hence it appears that bromine can displace chlorine from its compounds with oxygen, whilst chlorine can liberate bromine from its compound with hydrogen. The bromates are decomposed by heat in the same way as the chlorates.

IODINE.

Symbol I, *Atomic Weight* 126·53, *Density* 126·53.—Iodine occurs combined with metals in sea-water, and is obtained from kelp, the ash of certain sea-weeds, in which it is found as the iodides of sodium and magnesium. It was discovered in 1812 by Courtois. Iodine is obtained from kelp by exactly the same process as that by which chlorine and bromine are obtained from chlorides and bromides, viz. by heating with sulphuric acid and manganese dioxide. At the present time, iodine is chiefly prepared from the so-called "caliche," which is the crude sodium nitrate found in Peru and Chili. The mother liquors obtained in preparing the pure Chili saltpetre, contain considerable quantities of iodine in the form of sodium iodate. Iodine forms a deep violet-coloured vapour (*ἰωειδής*) which condenses to a dark grey solid, with a bright metallic lustre. Iodine melts at 115°, and boils above 200°, and has a specific gravity of 4·95; it gives off a perceptible amount of vapour at the ordinary temperature and possesses a faint chlorine-like smell. When the vapour of iodine is heated to temperatures above 700°, its density diminishes as the temperature increases, until at a temperature of 1400° the density becomes constant, one volume of the vapour weighing 63·26, or half its original amount. This shows that the vapour at 1400° consists of free atoms of iodine (see *ante*, *p. 57*), so that its molecular formula at that temperature is I, Water dissolves a very small quantity of iodine; but in presence of a soluble iodide it is freely dissolved, forming a deep red or brown solution: it is easily soluble in alcohol, giving a reddish-brown solution, and also in carbon disulphide and chloroform, imparting to them a splendid violet colour. Iodine does not possess such active properties as either of the preceding elements, its solution does not bleach organic colouring matters, and it is liberated from its compounds by both bromine and chlorine. Free iodine forms a remarkable compound with starch, of a splendid *blue* colour; and by this means the minutest trace of either substance can be detected. To apply this test, one drop of potassium iodide solution is added to starch paste largely diluted with water; no blue colour is observed until the iodine is set free by the addition of a drop or two of chlorine-water, when a deep blue coloration is instantly perceived. This coloration disappears on warming, or on addition of an excess of chlorine water. Iodine acts as a powerful poison; but given in small quantities, it is much used as medicine.

Hydriodic Acid, or *Hydrogen Iodide.*

Symbol HI, *Molecular Weight* 127·53, *Density* 63·76.—Iodine and hydrogen may be made to unite with each other by heating them together: hydriodic acid is liberated when dilute sulphuric acid acts on an iodide. This substance is, however, best prepared by acting upon phosphorus iodide with water, thus:

$$PI_3 + 3H_2O = 3HI + H_3PO_3.$$

Phosphorus tri-iodide and water produce hydriodic acid and phosphorous acid.

Hydriodic acid is a colourless gas, possessing a strong acid reaction, and fuming strongly in the air: it is very soluble in water, yielding a solution which boils at 127°, and contains 57 per cent. of HI. The gas liquefies under pressure, and solidifies at $-55°$. An analysis of this gas shows that hydriodic acid (like hydrochloric and hydrobromic) is composed of one volume of hydrogen and one of iodine vapour, forming two volumes of hydriodic acid.

Oxides and Oxy-acids of Iodine.

Iodine, when treated with solutions of caustic alkalis, does not yield bleaching liquors; nor is there any compound corresponding to hypochlorous acid known in the iodine series. It forms, however, two important acids, iodic and periodic acids, corresponding respectively with chloric and perchloric acids. Only one oxide of iodine, viz. I_2O_5, is known.

Iodic Acid, or *Hydrogen Iodate.—Symbol* HIO_3, *Molecular Weight* 175·41.—This acid, which corresponds closely to chloric acid, may be obtained by the direct oxidation of iodine by nitric acid, and also by acting upon iodine water with chlorine, thus:

$$I + 3H_2O + 5Cl = HIO_3 + 5HCl.$$

Iodine, water, and chlorine yield iodic acid and hydrochloric acid.

The iodates of the alkali metals are formed (together with the iodides of the metals employed) like the chlorates and bromates, by dissolving iodine in the caustic alkalis:

$$6I + 6KOH = KIO_3 + 5KI + 3H_2O.$$

Iodine and caustic potash give potassium iodate, potassium iodide, and water.

The whole of the iodine is converted into iodate if chlorine gas be passed into the solution, thus:

$$I + 6KOH + 5Cl = KIO_3 + 5KCl + 3H_2O.$$

Iodine, caustic potash, and chlorine yield potassium iodate, potassium chloride, and water.

Hence we see that oxygen combines with iodine to form an iodate in preference to forming a chlorate with chlorine. The iodates of the alkali-metals decompose on heating like the corresponding chlorates, yielding oxygen and an iodide, whereas the iodates of the heavy metals yield the metallic oxides, iodine and oxygen.

Iodine Pentoxide, or *Iodic Anhydride*, I_2O_5, is obtained as a white crystalline solid by heating iodic acid, HIO_3, to 170°.

Periodic Acid, or *Hydrogen Periodate*, $HIO_4,2H_2O$, can be obtained from the corresponding perchloric acid by the addition of iodine. It is a white crystalline solid body; which on heating splits up into iodine pentoxide, water and oxygen. The potassium salt of this acid, closely resembling the corresponding perchlorate, is obtained by passing chlorine gas through a solution of the iodate and caustic potash; thus:

$$KIO_3 + 2KOH + Cl_2 = KIO_4 + 2KCl + H_2O.$$

Iodine and Nitrogen.—The three atoms of hydrogen in ammonia can be wholly or partly replaced by iodine; the resulting compounds are black powders, which, when touched in the dry state, suddenly decompose with a loud report, and sometimes even explode spontaneously. The pure iodide of nitrogen is prepared by the action of a strong alcoholic solution of iodine upon aqueous ammonia, thus:

$$6I + 4NH_3 = NI_3 + 3NH_4I.$$

FLUORINE.

Symbol F, *Atomic Weight* 19·1.—This element occurs combined with the metal calcium, forming calcium fluoride, or fluorspar, CaF_2, a mineral crystallizing in cubes and found in Derbyshire: it also exists in large quantities in cryolite ($3NaF + AlF_3$), a mineral found in Greenland, whilst it has been detected in minute quantities in the teeth, and even in the blood, of animals. Fluorine has recently been isolated by the electrolysis of perfectly anhydrous hydrofluoric acid containing a little acid potassium fluoride to enable it to conduct electricity. The electrolysis can only be performed in perfectly dry platinum vessels. Fluorine is given off at the positive pole as a colourless gas which attacks almost all substances, organic and inorganic. Arsenic, antimony, sulphur, iron, and other elements, as well as cork and alcohol, ignite spontaneously in contact with the gas, and it decomposes water with formation of ozone and hydrofluoric acid.

Fluorine is remarkable as forming no compounds with oxygen.

Hydrofluoric Acid, or *Hydrogen Fluoride*.

Symbol HF, *Molecular Weight* 20·1, *Density* 10·05.—This gas corresponds in composition to the hydrogen compounds of the three preceding elements, and may be obtained in an exactly similar manner by the action of sulphuric acid upon calcium fluoride, thus:

$$H_2SO_4 + CaF_2 = 2HF + CaSO_4.$$

Sulphuric acid and calcium fluoride give hydrofluoric acid and calcium sulphate.

Hydrofluoric acid gas must be prepared in a leaden or platinum vessel, as glass is rapidly attacked by the vapour.

The colourless gas thus obtained fumes strongly in the air; if it be passed into a metallic tube placed in a freezing mixture at the temperature of $-20°$, a liquid is formed; this liquid still contains traces of water, which are removed by electrolysis, the fluorine formed decomposing the water into ozone and hydrofluoric acid. The anhydrous liquid boils at $19°\cdot5$. The strong acid acts very violently upon the skin, producing painful wounds; and the fumes of the gas are likewise dangerous from their corrosive power. When brought into contact with water the strong acid dissolves with a hissing noise; this aqueous acid attains a constant boiling point under the ordinary atmospheric pressure, when the liquid contains 37 per cent. of HF.

The most remarkable property of hydrofluoric acid is its power of etching upon glass: this arises from the fact that fluorine forms, with the silicon contained in the glass, a volatile compound called silicon tetrafluoride (see p. 141). This etching serves as a very delicate test of the presence of fluorine, and is effected in a very simple manner by covering a watch-glass with a thin coating of wax, removing a portion by means of a sharp point, and then exposing the glass for a short time to the vapour of hydrofluoric acid given off by heating the materials with sulphuric acid in a small leaden saucer; on removing the wax with a little turpentine, the marks on the glass will be distinctly visible. The solution of hydrofluoric acid in water is also used for the purpose of etching glass. Fluorspar is used in metallurgic operations as a flux, whence its name (*fluo*, I flow.)

The members of the foregoing group of elements exhibit certain remarkable relations among themselves, especially a gradation in properties. Thus fluorine and chlorine are gases, bromine is a liquid, and iodine a solid at ordinary temperatures; the specific gravity of liquid chlorine is 1·33, of bromine, 2·97, and of iodine 4·95; liquid chlorine is transparent, bromine but slightly so, and iodine is opaque. The combining weight, and therefore the vapour density, of bromine is nearly the mean of those of chlorine and iodine, $\frac{35·37+126·53}{2}=80·95$; and in its general chemical deportment bromine stands half-way between the other two elements. The property which distinguishes these substances from the rest of the elements is the power of forming, with hydrogen, compounds containing equal volumes of the constituent gases united without condensation.

LESSON XII.

SULPHUR.

Symbol S, *Atomic Weight* 31·98, *Density* 31·98.—Sulphur occurs both free and combined in nature: it is found free in certain volcanic countries, especially in Sicily and Iceland, and occurs crystallized in yellow transparent crystals in the form of rhombic octahedra (Fig. 38). It exists in combination with many metals, forming compounds termed sulphides, which constitute the common ores from which the metals are usually obtained: thus PbS, lead sulphide, or *Galena;* ZnS, zinc sulphide, or *Blende;* and CuS, copper sulphide, are the substances from which those metals are generally procured; it is also found combined with iron in large quantities, forming *iron pyrites*, FeS_2, which has, however, no value as iron-ore. Sulphur is also found in nature, combined with metals and oxygen, to form a class of salts called sulphates: of these, calcium sulphate or gypsum, $CaSO_4+2H_2O$, barium sulphate or heavy spar, $BaSO_4$, sodium sulphate or Glauber's salt, $Na_2SO_4+10H_2O$, occur in the largest quantity. Sulphur likewise occurs combined with hydrogen, as a gas called Sulphuretted Hydrogen, H_2S, in the waters of certain springs, as at Harrogate.

In order to obtain pure sulphur, the mineral containing the crude substance mixed with earthy impurities is placed in a round hole dug in the ground averaging from two to three meters in diameter and about half a meter in depth. Fire is applied to the heap in the evening, and in the morning a quantity of liquid sulphur is found to have collected at the bottom of the hole; this is then ladled out, the combustion being allowed to proceed further until the whole mass is burnt out. By this process only about one-third of the sulphur contained in the ore is obtained, the remaining two-thirds burning away and evolving clouds of sulphurous acid. When brought to this country, the sulphur thus obtained is refined or purified by subjecting it to distillation, the vapour being condensed in chambers, as shown in Fig. 39. If the vapour of sulphur is quickly cooled below its melting point, it solidifies in the form of a fine crystalline powder called Flowers of Sulphur, exactly as aqueous vapour, when cooled down below the freezing point of water, deposits as snow. When sulphur is gently heated, it melts, and may be cast into sticks, and is then known as brimstone or roll sulphur. Sulphur is also recovered in large quantities from the "alkali waste" obtained in the manufacture of soda (p. 193).

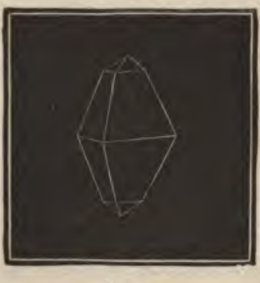

FIG. 38.

Sulphur exists in three modifications; the first is that in which sulphur crystallizes in nature, and the other two are obtained by melting sulphur. If melted sulphur be allowed to cool slowly, it crystallizes in long, transparent, needle-shaped, prismatic crystals, which are quite different in form from the natural crystals of sulphur, and have the specific gravity of 1·98; whereas the specific gravity of the crystals of native sulphur is 2·07. These transparent crystals become opaque after exposure to the air for a few days, owing to each crystal splitting up into several crystals of the natural octahedral, or permanent form. The third allotropic modification of sulphur is obtained by pouring melted sulphur heated to 230° into cold water: the sulphur thus forms a soft tenacious mass resembling caoutchouc, and has a specific gravity of 1·96. This form of sulphur is, however, not permanent; in a few hours, at the temperature of the air, the mass assumes the ordinary brittle form of the element, while, if heated to 100°, it instantly changes to the brittle form, and thereby evolves so much heat as to raise its temperature up to 111°. These peculiar modifications become apparent when sulphur is heated: thus, sulphur melts, to begin with, at 115°, and forms an amber-colour mobile liquid; as the temperature rises, the liquid becomes dark-coloured, and attains the consistency of thick treacle, so that at about 230° it can scarcely be poured out of the vessel; heated above 250°, it again becomes fluid, and remains as a dark reddish-black coloured thin liquid, until the temperature rises to 440°, when it begins to boil, and gives off a red-coloured vapour.

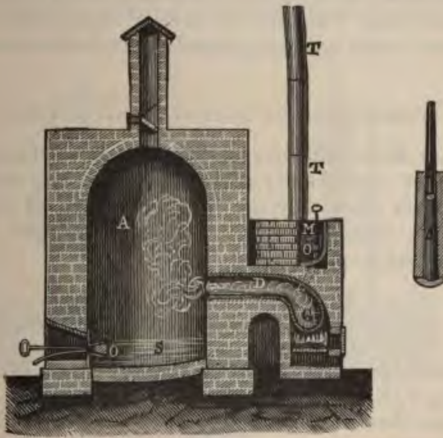

FIG. 39.

Sulphur is an inflammable substance, and when heated in the air or in oxygen burns with a bluish flame, combining with the oxygen to form sulphur dioxide (often called sulphurous acid), SO_2, which is given off as a gas, possessing a peculiar and well-known suffocating smell. Sulphur combines directly with chlorine, carbon, and most other elements, whilst many metals burn in its vapour as they do in oxygen gas, forming sulphides. Sulphur is insoluble in water and most organic liquids, but both the natural octahedral variety and the other crystalline (or prismatic) variety dissolve freely in carbon disulphide, CS_2, whilst the tenacious form of sulphur is insoluble in this liquid. When deposited from solution in carbon disulphide, sulphur crystallizes in the ordinary natural or octahedral form.

COMPOUNDS OF SULPHUR AND OXYGEN

Sulphur forms with oxygen two compounds belonging to the class of *acid-forming* oxides, that is, oxides which give rise to acids when they are brought in contact with water. These are *Sulphur Dioxide*, SO_2, and *Sulphur Trioxide*, SO_3, yielding respectively—

H_2SO_3, Sulphurous Acid, and
H_2SO_4, Sulphuric Acid.

In addition to these, the sesquioxide, S_2O_3, and the peroxide, S_2O_7, or S_2O_8, are known.

Besides these, six other oxy-acids of sulphur exist, with whose corresponding oxides we are unacquainted. The following list gives the composition of the eight sulphur oxyacids : numbers 2, 3, and 4, are important compounds; the remaining bodies are but little known, and do not as yet serve any purpose in the arts or manufactures. These compounds exhibit in a striking manner the law of multiple combining proportions enunciated by Dalton. (See *ante*. p. 55).

Oxy-acids of Sulphur.

(1) Hyposulphurous Acid. . . $H_2S\ O_2$.
(2) Sulphurous Acid. . . . . $H_2S\ O_3$.
(3) Sulphuric Acid . . . . . $H_2S\ O_4$.

(4) Thiosulphuric Acid . . .	$H_2S_2O_3$.
(5) Dithionic Acid	$H_2S_2O_6$.
(6) Trithionic Acid	$H_2S_3O_6$.
(7) Tetrathionic Acid . . .	$H_2S_4O_6$.
(8) Pentathionic Acid . . .	$H_2S_5O_6$.

Sulphur Dioxide, or *Sulphurous Anhydride*.[1]

Symbol SO_2, *Molecular Weight* 63·9, *Density* 31·95.—This gas is obtained when sulphur is burnt, and it is given off in large quantities from volcanic craters; it may be prepared more conveniently on the small scale by removing the elements of water, and one additional atom of oxygen from sulphuric acid by heating it together with the metals copper or mercury, thus:

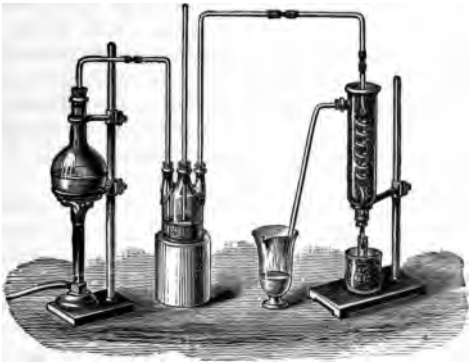

FIG. 40.

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O.$$

Copper and sulphuric acid yield sulphide dioxide, copper sulphate, and water.

The gas thus given off may be washed to purify it, and then collected over mercury or by displacement. It is a colourless gas, possessing a suffocating smell of burning sulphur; it is 2·211 times heavier than air, and may be condensed to a colourless liquid by cooling down to −8° under the ordinary atmospheric pressure; when cooled below −76°, the liquid freezes to a transparent solid. The arrangement for liquefying the gas is seen in Fig. 40: it consists of the usual evolution flask and washing bottle, which is connected with a spiral glass tube surrounded by a freezing mixture of salt and pounded ice. The gas condenses in this tube and falls down into the small flask placed below, which is also placed in a freezing mixture. When a sufficient quantity of the liquid has been collected, the neck of the flask can be sealed up by the blowpipe at the narrow part, and the liquefied sulphur dioxide preserved. This liquid evaporates very quickly when brought into the air, and the heat which thus becomes latent is so considerable, that the temperature may in this way be reduced to −50°: this is easily shown by pouring some of the liquid upon the bulb of an alcohol thermometer which has been wrapped in cotton-wool.

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[1] By anhydride is meant an oxide which forms an acid on treatment with water.

Sulphur dioxide, like all other gases which are easily condensed, exhibits considerable deviation from Boyle's law of pressures, occupying for equal increments of pressure less space than air under the same conditions; this difference becoming larger the lower the temperature.

The volume of this gas formed by the combustion of sulphur is found to be exactly the same as that of the oxygen employed. Hence, as the density of sulphur dioxide is 31·95, it contains equal weights of its constituent elements, 1 volume of sulphur uniting with 2 volumes of oxygen to give 2 volumes of the dioxide.

Sulphur dioxide is very soluble in water, 1 volume of water at 10° dissolving 51·38 volumes, and at 20° 39·37 volumes of this gas. The solution of the gas in water consists of *hydrogen sulphite*, or *sulphurous acid*, H_2SO_3, as the solution of carbon dioxide in water (p. 82) consists of the true carbonic acid: but this substance is decomposed on boiling the liquid, water and sulphur dioxide being reproduced, the latter escaping as a gas. If the solution of this gas in water be cooled below 5°, a crystalline hydrate of sulphurous acid separates out, having the composition $H_2SO_3+14H_2O$.

Sulphurous acid is the hydrogen salt of a series of compounds called sulphites: these compounds are easily decomposed by the stronger acids, sulphur dioxide being liberated as a gas. This substance is largely used as a bleaching agent, especially for silk and woollen goods which cannot be bleached by chlorine; it is also employed as an *antichlor* for the purpose of getting rid of the excess of chlorine present in the bleached rags from which paper is made.

In its bleaching action, sulphur dioxide acts in a manner exactly opposite to that in which chlorine acts, inasmuch as it unites with the oxygen of the water or colouring-matter present, forming sulphuric acid and liberating the hydrogen; so that sulphurous acid bleaches by acting as a reducing or deoxidizing agent, whereas chlorine bleaches by oxidation; similarly, its action as an antichlor depends on the formation of sulphuric and hydrochloric acids, thus:

$$SO_2 + 2H_2O + 2Cl = H_2SO_4 + 2HCl.$$

The great value of sulphur dioxide in the arts is in the manufacture of sulphuric acid or oil of vitriol, and for this purpose enormous quantities of the dioxide are produced.

Sulphurous acid, H_2SO_3, like carbonic acid, H_2CO_3, is a dibasic acid; that is, it contains two atoms of hydrogen, both of them capable of being replaced by metals. Thus two classes of salts exist; the so-called *acid salts*, in which only one atom of hydrogen has been replaced, and the *normal salts*, in which both atoms have been replaced by a metal. Thus Hydrogen Potassium Sulphite, $HKSO_3$, is an acid salt, and Potassium Sulphite, K_2SO_3, is a normal salt. Similarly, we have Hydrogen Potassium Carbonate, $HKCO_3$, and Potassium Carbonate, K_2CO_3.

Sulphur Sesquioxide, S_2O_3, is a blue crystalline solid obtained by adding flowers of sulphur to sulphur trioxide, SO_3.

Sulphur Peroxide, S_2O_7, (or S_2O_8) is an oily liquid obtained by the action of a powerful electric current on a mixture of sulphur trioxide and oxygen. Neither of these oxides give rise to peculiar acids on treatment with water, nor are they used in the arts.

LESSON XIII

Sulphur Trioxide, or *Sulphuric Anhydride.*

Symbol SO_3, *Molecular Weight* 79·86, *Density* 39·93.—Sulphur dioxide does not, under ordinary circumstances, combine directly with oxygen to form SO_3, but if these two dry gases be passed together over heated and finely divided metallic platinum, union takes place, and dense white fumes of sulphur trioxide are evolved, condensing to long prismatic crystals melting at 15°, and boiling at 46°. On standing, these crystals change to long silky needles, fusing at 50°, and gradually solidifying to the prismatic modification. The trioxide yields a colourless vapour, which when passed through a red-hot tube is decomposed into two volumes of sulphur dioxide and one volume of oxygen. Sulphur trioxide does not redden litmus paper, and may be moulded by the dry fingers without charring the skin: when brought into contact with water, the two substances combine with great force, hissing as a red-hot iron would do, and forming sulphuric acid, H_2SO_4. The combination thus formed cannot be separated again into sulphur trioxide and water by boiling. The trioxide may likewise be prepared by distilling fuming sulphuric acid, $H_2S_2O_7$ (see below).

Sulphuric Acid, or *Hydrogen Sulphate.*

Symbol H_2SO_4, *Molecular Weight* 97·82.—This substance is the most important and useful acid known, as by its means nearly all the other acids are prepared, and also because it is very largely used in the arts and manufactures for a great variety of purposes. So valuable are the applications of this acid, that the quantity now manufactured in the South Lancashire district alone exceeds 3,000 tons per week. Indeed, it has been truly said that the commercial prosperity of a country may be judged of with great accuracy by the amount of sulphuric acid which it consumes.

Sulphuric acid was first prepared by distilling a compound of iron, oxygen, sulphur, and water, called ferrous sulphate or green vitriol. The acid thus obtained is known as *fuming* or *Nordhausen* acid, and contains a compound of hydrogen sulphate and sulphur trioxide, $H_2SO_4 + SO_3$, or $H_2S_2O_7$, to which the name of *pyrosulphuric acid* has been given.

Manufacture of Sulphuric Acid.—The above plan of preparation has, however, long been superseded by the following more convenient method, which depends upon the fact that, although sulphur dioxide does not combine with free oxygen and water to form sulphuric acid, it is capable of taking up the oxygen when the latter is united with nitrogen in the form of nitrogen trioxide, N_2O_3, thus :

$$SO_2 + H_2O + N_2O_3 = H_2SO_4 + N_2O_2.$$

Sulphur dioxide, water, and nitrogen trioxide yield sulphuric acid and nitric oxide.

The nitric oxide formed in this decomposition takes up another atom of oxygen from the air, becoming N_2O_3, and this is again able to convert a second molecule of SO_2 with H_2O into H_2SO_4, being a second time reduced to N_2O_2, and ready again to take up another atom of oxygen from the air. Hence it is clear that the N_2O_2 acts simply as a carrier of oxygen between the air and the SO_2; an indefinitely small quantity of this nitrogen trioxide being, therefore, theoretically able to convert an indefinitely large quantity of sulphur dioxide, water, and oxygen into sulphuric acid.[1]

This process is carried on, on the large scale, in chambers (often of a capacity of 50,000 or 100,000 cubic feet) made of sheets of lead supported upon wooden beams and uprights, into which the above-mentioned materials are brought. Fig. 41 shows in a bird's-eye view the arrangements for the manufacture of sulphuric acid. The leaden chambers, of which two are represented in the figure, are connected together by a wide leaden passage, and the gases passing from the first into the second chamber thus become thoroughly mixed. The sulphur dioxide is procured either by burning sulphur in a current of air, or by roasting a mineral called iron pyrites (a

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[1] There is some doubt respecting the actual decomposition occurring in the leaden chamber, and the above must be taken only as a general explanation of what goes on. If the supply of steam be insufficient, a solid compound is formed, having the composition $SO_2\left\{\begin{matrix}NO_2\\OH\end{matrix}\right.$: this is decomposed, on addition of water, into sulphuric acid, nitric acid, and nitric oxide. This substance, which has been called the *crystals of the leaden chamber*, is supposed by some to play an important part in the formation of sulphuric acid.

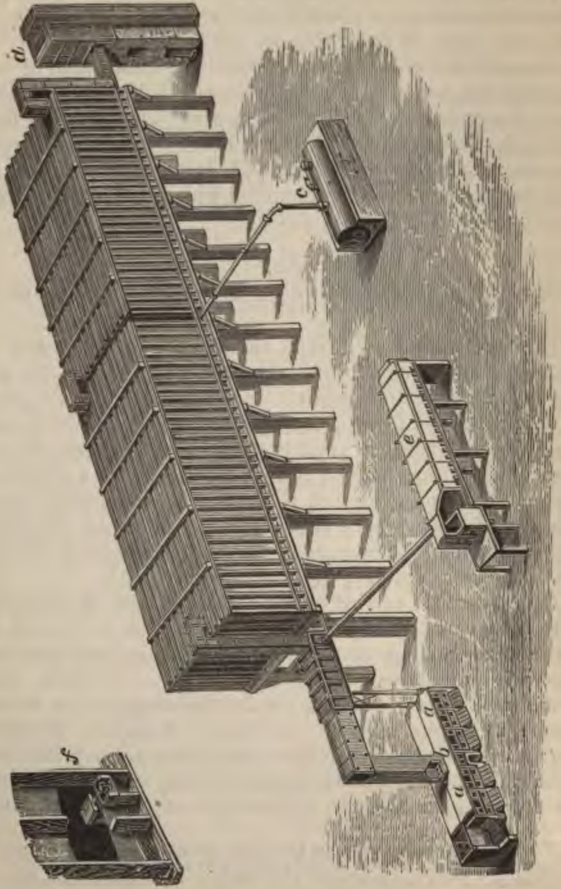

FIG. 41.

compound of sulphur and iron, FeS_2) in a suitable furnace (*aa*). The sulphur of the pyrites burns away and the gaseous product is led, together with atmospheric air, into the chamber, whilst ferric oxide, Fe_2O_3, remains behind in the furnace. A small stove (*b*), containing nitre, is placed in the central part of the furnace, where this salt is decomposed by the action of sulphuric acid which is poured upon it, a sulphate of potash being formed, whilst nitrous fumes pass with the other gases into the chamber. Jets of steam are also blown into the chamber at various points, from a boiler (*c*), and a thorough draught is maintained by connecting the end of the chamber with a high chimney not shown in the figure, but placed beyond the tower (*d*). The fumes, gases, and air escaping from the chamber have to pass through this tower (*d*), and there meet with a stream of concentrated sulphuric acid, by means of which the soluble acid vapours are nearly all condensed before reaching the chimney. The sulphuric acid, as it forms, falls on to the floor of the chamber, and when the process is working properly, it is continually drawn off, attaining a specific gravity of about 1·60, the strength being ascertained by an arrangement shown in (*f*), whilst the waste gases passing out of the chamber should contain nothing but nitrogen and small quantities of nitric oxide. In order to obtain from this weak chamber-acid the pure sulphuric acid, H_2SO_4, the excess of water must be removed by evaporation: this is conducted, on the large scale, first, by heating the chamber acid in covered leaden pans (*e*), until the specific gravity rises to 1·72, when the acid is known as the *brown oil of vitriol* of commerce, and then further concentrating in vessels of glass or of platinum (as lead is attacked by the strong acid), until its maximum strength and specific gravity is attained. Sulphuric acid thus obtained is a thick oily liquid boiling about 338°[1] and freezing at 10°·5; its specific gravity at 0° is 1·854. It combines with water with great energy, absorbing moisture rapidly from the air: hence it is used in the laboratory as a drying agent. Great heat is evolved when this acid is mixed with water, and care must be taken to bring these two liquids together gradually; otherwise an explosive combination may ensue. Many organic bodies, such as woody fibre and sugar, are completely decomposed and charred by strong sulphuric acid, whilst others, such as alcohol, oxalic and formic acid, are split up into other compounds by the withdrawal of the elements of water by this acid.

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[1] When boiled, hydrogen sulphate undergoes a slight decomposition, sulphur trioxide being evolved, and an acid remaining behind which contains only 98·4 to 98·8 of H_2SO_4, and which at 338° C. may be boiled down without further decomposition.

One molecule of hydrogen sulphate unites with one of water to form a compound, $H_2SO_4 + H_2O$, which can be obtained pure by cooling a mixture of acid and water having a specific gravity of 1·78 down to 7° C., at which temperature rhombic crystals of the hydrated acid are formed. The sulphuric acid of commerce frequently contains large quantities of impurities, especially lead sulphate from the chamber, and frequently arsenic from the pyrites, and nitric acid, as well as the lower oxides of nitrogen. In order to free the acid from these impurities, it must be distilled and subjected to other treatment, for a description of which the reader is referred to the larger treatises.

At high temperatures sulphuric acid decomposes into sulphur dioxide, SO_2, oxygen, O, and water, H_2O : thus, if a current of the acid be allowed to flow on to red-hot bricks, and the gases resulting from the decomposition passed through water, the sulphur dioxide will be completely absorbed, and a supply of pure oxygen obtained.

Hydrogen sulphate is a dibasic acid, and therefore in the case of the alkali-metals, we have two salts, thus—Hydrogen potassium sulphate, $KHSO_4$, and normal potassium sulphate, K_2SO_4. Barium and lead sulphates are insoluble in water: hence soluble salts of these metals are used as tests of the presence of a sulphate, a few drops of solution of barium chloride, for example, producing, in presence of hydrochloric acid, an immediate white precipitate of barium sulphate in water containing the merest trace of sulphuric acid or of a soluble sulphate:

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl.$$

Calcium, strontium, and mercury and silver sulphates are but slightly soluble in water, whilst the other sulphates are easily soluble.

Some sulphates crystallize as anhydrous salts, such as K_2SO_4, potassium sulphate; $BaSO_4$, barium sulphate; and Ag_2SO_4, silver sulphate: whilst others require water to retain their crystalline form, and this water is termed *water* *of crystallization.* The crystals of ferrous sulphate or green vitriol, and of zinc sulphate or white vitriol, contain seven molecules of water in the solid form; whilst copper sulphate or blue vitriol requires but five molecules to preserve its crystalline form, thus:

$$\begin{array}{l} FeSO_4 + 7H_2O \\ ZnSO_4 + 7H_2O \end{array} ; \text{ and } CuSO_4 + 5H_2O.$$

Thiosulphuric Acid, or *Hydrogen Thiosulphate* (*formerly called Hyposulphurous Acid*).

Symbol $H_2S_2O_3$.—This acid is not known in the free state. The formula of a metallic thiosulphate, such as that of sodium, is $Na_2S_2O_3$: this also contains five molecules of water of crystallization. It is largely used in photography for the purpose of fixing the image, the salt possessing the property of dissolving the silver salts which have been unacted on by the light. This useful salt, commonly known as hyposulphite of soda, is prepared by passing a current of sulphur dioxide into a mixed solution of sodium sulphide and caustic soda, and purifying by crystallization the sodium thiosulphate obtained:

$$2Na_2S + 2NaOH + 4SO_2 = 3Na_2S_2O_3 + H_2O.$$

Hyposulphurous Acid, or *Hydrogen Hyposulphite.*

Symbol H_2SO_2.— This compound is formed by the action of zinc on sulphurous acid:

$$Zn + 2SO_2 + H_2O = ZnSO_3 + H_2SO_2.$$

It consists of a yellow liquid, which acts as a far more powerful reducing agent than sulphurous acid, and at once bleaches vegetable colouring matters. Hyposulphurous acid readily undergoes decomposition with separation of sulphur. It forms a series of salts, which are stable in the dry state, but in solution are soon converted into thiosulphates.

Sulphur dioxide not only combines directly with oxygen to form SO_3, but also with chlorine to form SO_2Cl_2, *sulphuryl dichloride.* SO_3 not only combines with a molecule of water to form sulphuric acid, H_2SO_4, but also with a molecule of HCl to form SO_3HCl, *chlorosulphonic acid*, or *chlorhydrosulphuric acid.* This substance is of interest, because it is also produced by a reaction common to many bodies, which may, like the acids, be considered as one or more molecules of water in which one or more atoms of hydrogen have been replaced by a radical. If we bring together water and a compound of phosphorus and chlorine, PCl_5, we obtain hydrogen chloride and phosphorus oxychloride:

$$PCl_5 + H_2O = POCl_3 + 2HCl;$$

and if phosphorus pentachloride be added to concentrated sulphuric acid, the reaction occurs in two stages:

$$(1)\ PCl_5 + H_2SO_4 = POCl_3 + HCl + SO_3HCl.$$
$$(2)\ PCl_5 + SO_3HCl = POCl_3 + HCl + SO_2Cl_2.$$

It will be seen that in both these reactions, one atom of hydrogen and one of oxygen are taken out, and one atom of chlorine substituted for the group of atoms OH (termed the *radical hydroxyl*). Sulphuric acid may, however, be regarded as two molecules of water in which two atoms of hydrogen are replaced by the group SO_2, called *sulphuryl.*

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 \quad \text{or} \quad \begin{matrix}HOH\\HOH\end{matrix} \qquad SO_2\begin{matrix}OH\\OH.\end{matrix}$$

Expressed according to this last formula we can plainly see the relations existing between the compounds derived from the oxides of sulphur.

$SO.O$	$SO\left\{\begin{matrix}OH\\OH\end{matrix}\right.$	$SO_2\{O$	$SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$
Sulphur Dioxide.	Sulphurous Acid.	Sulphur Trioxide.	Sulphuric Acid.
$SO_2\left\{\begin{matrix}OH\\SH\end{matrix}\right.$	$SO_2\left\{\begin{matrix}OH\\Cl\end{matrix}\right.$	$SO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	$SO_2\left\{\begin{matrix}OH\\NO_2\end{matrix}\right.$
Thiosulphuric Acid.	Chlorosulphonic Acid.	Sulphuryl Chloride.	Crystals of the Leaden chamber.

COMPOUNDS OF SULPHUR AND HYDROGEN.

Two of these are known—viz., hydrogen sulphide, H_2S, and hydrogen disulphide, H_2S_2.

Hydrogen Sulphide, or *Sulphuretted Hydrogen.*

Symbol H_2S, *Molecular Weight* 33·98, *Density* 16·99.—This gas is formed when hydrogen is led through boiling sulphur, but it is best prepared by the action of dilute sulphuric acid upon ferrous sulphide (sulphide of iron), FeS, ferrous sulphate being also formed :

$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$

here two atoms of hydrogen change place with one of divalent iron. Fig. 42 represents a convenient form of apparatus for the production and purification of this gas. It may be collected over warm water, and is a colourless gas, possessing the peculiar odour of rotten eggs; it burns on application of a light with a bluish flame, forming water and sulphur dioxide. When inhaled, it acts as a poison on the animal economy, even if diluted with large quantities of air. Sulphuretted hydrogen gas dissolves in water to a considerable extent, imparting its peculiar smell and a slightly acid reaction to the water. One volume of water at 0° dissolves 4·37 volumes of the gas, while at 15° 3·23 volumes are absorbed. Exposed to a temperature of $-62°$, this gas condenses to a colourless mobile liquid, which, when further cooled to $-85°$, freezes to a transparent ice-like solid. At a pressure of about seventeen atmospheres this gas also liquefies under

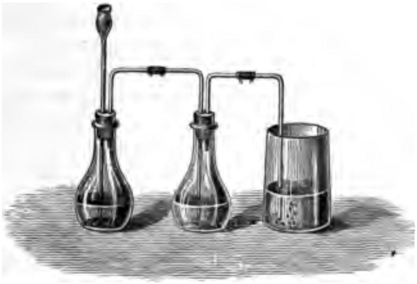

FIG. 42.

the ordinary temperature of the air. Sulphuretted hydrogen occurs free in nature in volcanic gases, as well as in the water of certain springs; thus Harrogate waters owe their peculiar odour to the presence of this gas. It is likewise generated by the putrefaction of animal matters, such as albumen, or the white of eggs, which contains sulphur; also by the deoxidation of sulphates in presence of decaying organic matter.

The composition of sulphuretted hydrogen may be ascertained either by heating a small piece of metallic tin in a known volume of the gas when tin sulphide will be formed, and hydrogen liberated; or by decomposing the gas by means of a red-hot platinum wire, when the whole of the sulphur is deposited and hydrogen set free. In both cases the volume of hydrogen obtained is found to be equal to that of the gas employed; and hence 2 volumes of sulphuretted hydrogen, weighing 33·98, consist of 2 volumes of hydrogen weighing 2, and 1 volume of sulphur vapour, weighing 31·98.

Sulphuretted hydrogen is an invaluable reagent in the laboratory, as by its means we are enabled to separate the metals into groups. If we pass a current of this gas through a solution of a copper salt, to which a small quantity of acid has been added, we obtain an immediate precipitate of copper sulphide:

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

If we do the same with a solution of an iron salt, we get no such precipitate, because iron sulphide is soluble in an acid; but on the addition of an alkali, iron sulphide is at once precipitated:

$$FeSO_4 + 2KOH + H_2S = FeS + K_2SO_4 + 2H_2O.$$

We may thus divide the metals into groups; first, those which, like copper, are precipitated by sulphuretted hydrogen from an acid solution, or the *copper group*; second, those which are not precipitated by sulphuretted hydrogen in an acid solution, but which are so precipitated in an alkaline one, or the *iron group*; and third, those which are in no case precipitated by this reagent, as their sulphides are soluble in water, acids or alkalis (to this group belong the metals of the *alkalis and alkaline earths*).

Sulphuretted hydrogen is recognized by its peculiar odour, and by the fact that it gives a beautiful purple colouration with an alkaline solution of sodium nitroprusside.

Hydrogen Disulphide.

This substance is obtained by pouring a solution of calcium disulphide into hydrochloric acid:

$$CaS_2 + 2HCl = H_2S_2 + CaCl_2.$$

An oily liquid falls to the bottom of the vessel, which is the body in question. Hydrogen disulphide closely resembles hydrogen dioxide in many of its properties; it possesses a peculiar smell, bleaches, and readily decomposes into sulphur and sulphuretted hydrogen.

Carbon Disulphide.

Symbol CS_2, *Molecular Weight* 75·92, *Density* 37·96.—If the vapour of sulphur be passed over red-hot charcoal, a volatile compound, CS_2, is formed which may be condensed to a heavy colourless liquid, usually possessing a peculiarly disagreeable smell, boiling at 46°, and having a specific gravity of 1·292. Carbon disulphide is very inflammable, its vapour igniting at 149° when mixed with air, forming carbon dioxide and sulphur dioxide. It is insoluble in water, but acts as a solvent upon gums, caoutchouc, sulphur, and phosphorus; its vapour is, however, very poisonous, and it must be employed with caution. When perfectly pure it has a pleasant ethereal smell, the unpleasant odour of the commercial article being due to impurities.

A remarkable analogy is presented by the foregoing sulphur compounds and the corresponding bodies in the oxygen series; thus:—

Water, H_2O.	Sulphuretted Hydrogen, H_2S.
Hydrogen dioxide, H_2O_2.	Hydrogen disulphide, H_2S_2.
Carbon dioxide, CO_2.	Carbon disulphide, CS_2.

These possess not only an analogous composition, but similar chemical properties, whilst similar relations are seen in many other compounds of oxygen and sulphur.

Chlorine and Sulphur.—These elements unite directly to form the compounds SCl_4, SCl_2, and S_2Cl_2: they are formed by leading a current of chlorine gas over melted sulphur, and are volatile liquids, the tetra-chloride existing only at temperatures below $-22°$ and decomposing into SCl_2 and Cl_2, whilst the dichloride again yields on boiling $S_2Cl_2 + Cl_2$.

LESSON XIV

SELENIUM [1]

Symbol Se, *Atomic Weight* 78·0, *Density* 78·0.—Selenium is an element which closely resembles sulphur in its properties, but it occurs in very small quantities; it was discovered by Berzelius, who found it accompanying sulphur in certain varieties of Swedish pyrites. Selenium also occurs free in nature, and is found in combination with metals in certain rare minerals. Like sulphur it is capable of existing in two allotropic modifications, one of which is soluble in carbon disulphide, the other insoluble: the soluble form is precipitated when a solution of selenious acid is acted upon by a reducing agent; the insoluble modification results from the cooling of melted selenium. The specific gravity of the former variety is 4·5: that of the latter, 4·8. Selenium melts at 217°, and boils at a temperature below a red heat, giving off a deep yellow vapour. In a finely divided state, and when seen by transmitted light, selenium has a red colour. It burns in the air with a bright blue flame, which, when examined by means of the spectroscope (p. 269), exhibits a series of magnificent and characteristic bands. The smell of burning selenium is very peculiar, resembling that of rotten cabbages, and is due to the formation of an oxide the composition and properties of which are, however, as yet unknown. Only one oxide of selenium is known, viz., *selenium dioxide*, SeO_2, but two oxy-acids of selenium exist, viz. selenious acid H_2SeO_3, and selenic acid H_2SeO_4. These form well-defined salts termed the selenites and selenates which closely resemble the analogous sulphites and sulphates.

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[1] From σελήνη, the moon.

Selenium Dioxide and Selenious Acid, or *Hydrogen Selenite. Symbol* SeO_2, *Molecular Weight* 109·92.—The dioxide is formed when selenium is burnt in the air, or in pure oxygen. It may be also prepared by oxidizing selenium in nitric acid or aqua regia. It is a white crystalline mass, capable of dissolving in water, and thus forming *selenious acid*, H_2SeO_3. From this solution selenium is at once deposited on addition of sulphurous acid, sulphuric acid being formed:

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

The metallic selenites correspond closely with the sulphites.

Selenic Acid, or *Hydrogen Selenate. Symbol* H_2SeO_4.—This is best prepared by fusing a selenite with nitre: on addition of a lead salt to the solution of the mass thus obtained, insoluble lead selenate is precipitated; this salt is decomposed by sulphuretted hydrogen, yielding selenic acid and lead sulphide:

$$PbSeO_4 + H_2S = H_2SeO_4 + PbS.$$

On evaporating the liquid obtained on filtration, selenic acid is left.

Selenic acid decomposes, on heating, into selenium dioxide, oxygen, and water; the metallic selenates correspond to the analogous sulphates, and are *isomorphous* with them, that is, they crystallize in the same forms and have an analogous composition. The most important difference between the two elements, sulphur and selenium, is that the former is oxidized to its highest point by the action of nitric acid, whereas the latter requires to be fused with nitre in order to reach the corresponding degree of oxidation.

Seleniuretted Hydrogen, or *Hydrogen Selenide.*

Symbol H_2Se, *Molecular Weight* 80·0, *Density* 40·0.—This gas is obtained by the action of an acid upon a selenide exactly as sulphuretted hydrogen is prepared from a sulphide. It is a colourless inflammable gas, possessing a nauseous smell, and exhibiting properties in every respect analogous to those of its sulphur representative.

TELLURIUM.[1]

Symbol Te, *Atomic Weight* 125, *Density* 125.—Tellurium is a very rare substance, which, although resembling a metal in its physical properties, bears so strong an analogy to sulphur and selenium in its chemical relations that its compounds are best considered in this place. It occurs combined with gold and other metals in Transylvania and Hungary. The specific gravity of tellurium is 6·24, and it exhibits a bright white metallic lustre. It melts at 452°, and may be volatilized at a white heat in a current of hydrogen gas. When heated in the air it burns with a bluish-green flame, forming white fumes of *tellurium dioxide*, TeO_2; this compound is also formed when tellurium is oxidized by nitric acid, and the solution evaporated to dryness. With water the dioxide forms *tellurous acid*, H_2TeO_3, and with metals in place of hydrogen, tellurites of the general form, M_2TeO_3. When tellurium or a *tellurite* is fused with nitre, potassium tellurate, K_2TeO_4, is formed, from which *telluric acid*, $H_2TeO_4 + 2H_2O$, and *tellurium trioxide*, TeO_3, can be obtained. With hydrogen tellurium forms a colourless gas, *telluretted hydrogen*, H_2Te, which cannot be distinguished by its smell from sulphuretted hydrogen.

Oxygen, sulphur, selenium, and tellurium form a natural group of elements, each uniting with two atoms of hydrogen to produce a series of bodies possessing analogous properties, viz. H_2O, H_2S, H_2Se, H_2Te. The last three members of the group exhibit the same kind of striking gradation of properties as was noticed in the case of chlorine, bromine, and iodine. Thus the mean of the combining weights of the two extremes is nearly the combining weight of the mean,

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[1] From *tellus*, the earth.

$$\frac{31{\cdot}98 + 128}{2} = 79{\cdot}9\,;$$

whilst their specific gravities, 2·0, 4·5, and 6·24, and their melting and boiling points, show a similar gradation.

SILICON.

Symbol Si, *Atomic Weight* 28.—Silicon, next to oxygen, is the most abundant element known. It does not occur, however, in the free state, but always combined with oxygen to form silicon dioxide (silicic acid or silica). Silicon dioxide exists nearly pure in quartz or rock-crystal, in flint, sand, and in a variety of minerals. Silicon also occurs combined with metals and oxygen, forming metallic silicates; and of these the greater part of almost all known rocks, especially the primary rocks, is composed.

In order to obtain silicon in the free state, a compound of this substance with fluorine and potassium, potassium silicofluoride, is heated with metallic potassium:

$$K_2SiF_6 + 4K = 6KF + Si.$$

A violent reaction occurs; and when the contents of the tube in which the decomposition has been effected are put into water, silicon is left undissolved in the form of a brown amorphous powder. It is however much more readily obtained by heating quartz-sand with magnesium powder, and extracting the silicon from the pulverized mass by melted zinc. On treatment of the zinc-silicon compound with acid, silicon remains behind in beautiful steel-blue needles, which have a specific gravity of 2·49, and are hard enough to scratch glass. These may be fused at a temperature above the boiling point of zinc.

Silicon Dioxide, or *Silica*.

Symbol SiO_2, *Molecular Weight* 59·92, is the only known oxide of silicon; it occurs in the pure state crystallized in six-sided prisms or pyramids, as quartz, and also in a second distinct crystalline form as tridymite. Amorphous silica is also found in nature as opal. Chalcedony, flint, and agate are mixtures of amorphous silica with quartz and tridymite. The aluminum, potassium, calcium, and iron silicates, mixed together in different proportions, constitute a large number of minerals.

Crystallized silica, in the form of a white transparent quartz, has a specific gravity of 2·6, and is hard enough to scratch glass ; it is unattacked and undissolved by all acids, with the exception of hydrofluoric acid, by the action of which silicon tetrafluoride and water are produced :

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

Tridymite has a specific gravity of 2·3, and the same hardness as quartz.

Silica is infusible except at the highest temperature of the oxyhydrogen blowpipe, when it melts to a colourless globule ; it cannot be vaporized at any known temperature. Silica in an amorphous condition can also be prepared, and then exhibits peculiar properties. To obtain it one part of finely-divided quartz or white sand is heated with four parts of sodium carbonate : as soon as the latter begins to fuse, the silica combines with the sodium and oxygen contained in the carbonate, forming a sodium silicate, called soluble glass, an effervescence of carbonic acid gas also taking place. If the fused mass be boiled with water, it will dissolve, and on the addition of hydrochloric acid, *silicic acid* or *hydrogen silicate*, H_4SiO_4, partly separates as a gelatinous mass, partly remains dissolved in the liquid. If this solution be evaporated to dryness, heated slightly, and hydrochloric acid then added, silicon dioxide is left as a white powder, insoluble in acids : this amorphous silica possesses a specific gravity of 2·2 to 2·83, and can only be obtained again in solution by repeating the process of fusion with an alkali, &c. A pure aqueous solution of *hydrogen silicate* can be obtained by allowing the solution of this substance in hydrochloric acid to diffuse through a membrane for some days. For this purpose the solution is brought into a flat drum or sieve made out of parchment paper, and this is allowed to float for some time in a large quantity of water. The hydrochloric acid and sodium chloride pass through the parchment paper, and a clear solution of pure silicic acid remains behind. The limpid liquid thus obtained may be concentrated by evaporation until the quantity of silicic acid in solution rises to 14 per cent.; but this solution is apt to gelatinize on standing, forming a clear jelly-like mass. This mode of separating chemical substances is termed *dialysis*, and it depends upon the fact that all crystallizable substances (called *crystalloids*) can pass in solution through the parchment paper, whilst all gum-like amorphous substances (*colloids*), such as the gelatinous silicic acid, cannot pass through.

Potassium and sodium silicates are largely used for various purposes in the arts, whilst mixtures of these with silicate of calcium or lead form the several descriptions of glass (p. 231).

Silicon Hydride.

Symbol SiH_4, is a colourless gas formed by the action of hydrochloric acid upon a compound of magnesium and silicon. It takes fire on coming into contact with the air, burning with a white flame, and forming water and silica, the latter substance separating out in the form of a white ring-shaped cloud.

Silicon Tetrachloride.

Symbol $SiCl_4$, *Molecular Weight* 169·48, *Density* 84·74.—This compound is formed when silicon is heated in chlorine, but may be prepared by passing dry chlorine over the product of the reaction of magnesium powder on silica, or over a red-hot mixture of finely-divided silica and carbon. Chlorine alone is not able to decompose silica, but in presence of carbon a change is effected, carbon monoxide being at the same time formed:

$$SiO_2 + Cl_4 + C_2 = SiCl_4 + 2CO.$$

Silica, chlorine, and carbon yield silicon tetrachloride and carbon monoxide.

Fig. 43 shows the arrangement employed for preparing this compound. One of the above-named mixtures is placed in a porcelain tube, which can be strongly heated by the furnace; dry chlorine gas is passed through the tube, and the volatile silicon chloride collects in the cool tube, dropping into the bottle placed below to receive it. Silicon chloride is a volatile colourless liquid, boiling at 59·6° C. and having a specific gravity of 1·52. It is at once decomposed by water, silicic and hydrochloric acids being formed: hence we may see that this body in the chlorine series corresponds to silicon dioxide in the oxygen series, and that in the formation of the chloride four atoms of chlorine simply replace the equivalent quantity, two atoms, of oxygen in the silica: SiO_2 becomes $SiCl_4$, as one atom of oxygen is equivalent to two of chlorine. Two other chlorides, viz., Si_2Cl_6 and Si_2Cl_4, have been prepared by passing the vapour of the tetrachloride over heated silicon.

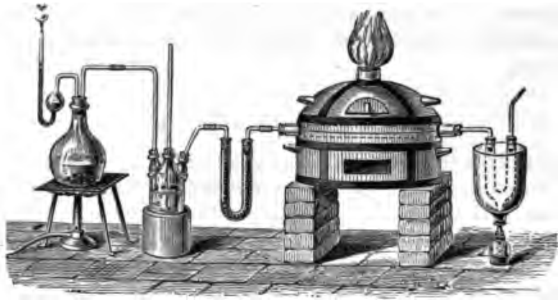

FIG. 43.

If dry hydrochloric acid gas be passed over heated silicon, another substance is formed together with silicon tetrachloride, to which the name of *silico-chloroform* has been given, because its constitution is similar to that of chloroform. This body is $SiHCl_3$, chloroform being $CHCl_3$, and it boils at 36°. It is very inflammable, and burns with a greenish flame, evolving dense white clouds of silica. It is also easily decomposed by water, and at low temperatures a white powder is formed, having the composition $Si_2H_2O_3$, called *silico-formic-anhydride:*

$$2SiHCl_3 + 3H_2O = \left.\begin{matrix}SiHO\\SiHO\end{matrix}\right\}O + 6HCl.$$

By acting on white-hot felspar with silicon tetrachloride, an oxychloride of silicon $\left.\begin{matrix}\mathrm{Si\,Cl_3}\\\mathrm{Si\,Cl_3}\end{matrix}\right\}\mathrm{O}$ is formed. This is a colourless strongly-fuming liquid, boiling at 137°, which, in contact with water, decomposes into hydrochloric and silicic acids. Four other oxychlorides of silicon have recently been prepared.

Silicon Tetrafluoride.

Symbol SiF_4, *Molecular Weight* 104·4, *Density* 52·2.—This is one of the most singular compounds of silicon. It is a gas which is formed whenever free hydrofluoric acid comes in contact with either free or combined silica: this is the cause of the etching which hydrofluoric acid produces upon glass. Silicon tetrafluoride is best prepared by heating in a flask equal parts by weight of finely-powdered fluor spar and white sand, with about eight parts of sulphuric acid: the decomposition first occurring is the one by which hydrofluoric acid is generated, and this, then, attacks the silica:

$$(1)\ CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$
$$(2)\ 4HF + SiO_2 = 2H_2O + SiF_4.$$

Silicon tetrafluoride is a colourless gas which fumes strongly in the air; it does not burn nor support combustion, and may be condensed by great pressure or on exposure to a very low temperature, to a colourless liquid; it is decomposed by water, but may be collected over mercury or by displacement. When led into water this gas yields silicic acid, which is deposited in a state of fine division, and another acid called *hydro-fluo-silicic acid*, or hydrogen silico-fluoride, having the composition H_2SiF_6, which remains in solution:

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4.$$

This latter substance has an acid reaction: the corresponding potassium and barium silico-fluorides (K_2SiF_6 and $BaSiF_6$), are insoluble in water and alcohol.

BORON.

Symbol B, *Atomic Weight* 11·0.—Boron combined with oxygen and sodium is found as *borax* in nature; it is also found combined with oxygen alone as ***boron trioxide***. It exists in two forms, crystalline and amorphous. Boron is easily obtained as a grey amorphous powder, by heating fused boron trioxide, B_2O_3, with sodium. Crystallized boron is prepared by heating the amorphous form strongly with aluminium, this metal in the fused state having the property of dissolving boron, which separates out in nearly colourless crystals when the metal cools, just as the graphitoidal form of carbon does from its solution in iron on cooling (p. 78). Crystallized boron has a specific gravity of 2·68, and occurs in the form of octahedra, which are hard enough to scratch the ruby. In one specimen of these colourless crystals, which was analysed, some quantity of carbon was found to be present; hence carbon may, in some sense, be said to have been prepared artifically in the diamond modification. Boron burns when strongly heated in oxygen or in chlorine, forming the oxide or chloride: it is remarkable as being one of the few elements which unite directly with nitrogen, absorbing this gas when red-hot with evolution of light, forming boron nitride, BN.

Boracic or Boric Acid.

Symbol H_3BO_3, *Molecular Weight* 61·88.—In certain old volcanic districts in Tuscany constant jets of steam and gas escape from the earth. These steam jets, which are known as *fumeroles* or *soffioni*, contain small quantities of boric acid, which collect in the lagoons formed at the mouth of the jet. By means of the heat of natural steam jets the solution of boracic acid is concentrated, and the acid obtained by crystallization: about 2,000 tons of crude acid thus prepared are imported every year from Tuscany. Boron likewise occurs as tinkal or sodium borate in Thibet and in California.

Boric acid is obtained by decomposing a hot solution of *borax*, $Na_2B_4O_7+10H_2O$, with sulphuric acid; crystals separate out on cooling, having the composition HBO_2+H_2O. These crystals on heating lose water and pass into a fused glassy mass, consisting of *boron trioxide*, B_2O_3. Boric acid is slightly soluble in cold, and rather more soluble in hot water; it imparts a peculiar green tint to the blowpipe flame, which exhibits a characteristic series of bands when examined by means of the spectroscope. It possesses strong antiseptic properties and is used as a preservative for meat. Metallic borates are known, and likewise several combinations of these borates with boron trioxide. Thus sodium borate, or boric acid, in which the atom of hydrogen is replaced by sodium, is $NaBO_2+4H_2O$; whilst fused borax is this salt combined with boron trioxide, thus: $2NaBO_2+B_2O_3$ or $Na_2B_4O_7$. Compounds similar to this latter salt are known amongst the sulphates. Thus Nordhausen sulphuric acid is $H_2S_2O_7$ (see p. 125), and a sodium compound, $Na_2S_2O_7$, is known. Many of the metallic oxides are soluble in fused borax, giving coloured glasses. Hence this compound is largely used in the arts as a flux, and in the laboratory as a blow-pipe reagent.

Boron combines with chlorine to form a *trichloride*, BCl_3, and with fluorine to form a corresponding *trifluoride*, BF_3: both these compounds are prepared by methods similar to that adopted for the corresponding silicon compounds, to which, notwithstanding their different constitution, they bear a strong resemblance. The existence of a hydride of boron, BH_3, has lately been ascertained. Like silicon, boron also forms a borofluoride; hydrofluoboric acid (or hydrogen borofluoride) is HBF_4, and potassium borofluoride KBF_4.

LESSON XV

PHOSPHORUS

Symbol P, *Atomic Weight* 30·96, *Vapour Density* 61·92.[1]—Phosphorus does not occur free in nature, but is found in combination with oxygen and calcium in large quantities in the bodies, and especially the bones of animals, in the seeds of plants and also as the minerals phosphorite and apatite. When bones are burnt, a white solid mass is left behind;

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[1] The volume occupied by the atom of phosphorus weighing 30·96 is only half as large as that occupied by the atoms of each of the preceding elements: hence the atomic volume of phosphorus is ½, that of the preceding elements being 1. The molecule of phosphorus, therefore, consists of 4 atoms.

this is called calcium phosphate (phosphate of lime). Animals obtain the phosphate necessary for the formation of their tissues, &c., from plants. Plants, again, draw their supply from the soil, whilst soils derive their phosphates from small quantities existing in the oldest granite rocks, by the disintegration of which the fertile soils have been produced. In order to increase the natural fertility of soils, artificial manures containing phosphates are much used. Phosphorus appears also to be a very necessary ingredient in the brain and other centres of nervous action. It was accidentally discovered by Brand of Hamburg in 1669; but Scheele, in 1771, first pointed out the existence of phosphorus in the bones, and examined its properties carefully.

Phosphorus is prepared from powdered bone-ash, by mixing it with two-thirds of its weight of sulphuric acid and 15 to 20 parts of water. The sulphuric acid decomposes the bone-ash, forming calcium sulphate, or gypsum, which separates out as a white insoluble powder; whilst the greater part of the phosphorus in the bones comes into solution in combination with calcium, oxygen and hydrogen, forming calcium hydrogen phosphate, a salt commonly known as *superphosphate of lime*, and employed in manufacturing artificial manures. The liquid is drawn off clear, evaporated down to a syrup, and then mixed with powdered charcoal, dried, and heated to redness in an earthenware retort, the neck of which dips under water. The soluble phosphate is then converted into calcium metaphosphate, and this is decomposed on heating as shown in the equation:

$$\underset{\text{Calcium Metaphosphate.}}{3Ca(PO_3)_2} + 10C = P_4 + \underset{\text{Calcium Triphosphate.}}{Ca_3(PO_4)_2} + 10CO.$$

The phosphorus is liberated together with carbon monoxide, and distils over, collecting under the water in yellow drops, whilst the other third remains behind in the retort as calcium triphosphate.

Recently phosphorus has been prepared by the electrolysis at a very high temperature of phosphate of lime.

In order to purify the phosphorus manufactured by either of the above processes, it may again be distilled, or pressed when melted under hot water through leather; it is then cast into sticks and kept under cold water.

Phosphorus is an exceedingly inflammable and oxidizable substance, and requires great care in its preparation: it is manufactured on a very large scale for making the composition for the tips of lucifer-matches. Phosphorus is a slightly yellow semi-transparent solid, resembling white wax both in appearance and consistency: but at low temperatures it becomes brittle; it may be obtained in the crystalline form by distilling it in an atmosphere of carbonic anhydride. Its specific gravity is 1·83, and it melts at 44°·3, forming a transparent liquid: it boils at 290°, giving rise to a colourless gas. In the air it gives off white fumes, emitting a pale *phosphorescent* light in the dark—whence its name;[1] it is then undergoing a slow combustion, the white fumes consisting of *phosphorous oxide*, P_4O_6. At a temperature very little above its fusing point phosphorus takes fire in the air, entering into active combustion, and forming *phosphorus pentoxide*, P_2O_5 (or phosphoric anhydride). The ignition of phosphorus takes place by slight friction, or by a blow, and even the heat of the hand may cause this substance to ignite; hence great care must be taken in handling phosphorus, and it should always be cut under water. Phosphorus does not dissolve in water, alcohol, or ether, but it is slightly soluble in oils, and very readily soluble in carbon disulphide, crystallizing from its solution in this liquid in rhombic dodecahedra.

Allotropic Modifications of Phosphorus.—If yellow phosphorus be exposed to a temperature of about 240° for some hours in an atmosphere incapable of acting chemically on it (such as hydrogen or carbon dioxide), it is found to have undergone a very remarkable change, being wholly converted into a dark red opaque substance, altogether insoluble in carbon disulphide. The weight of red substance produced is exactly equal to that of yellow phosphorus used. This is called *red* or *amorphous phosphorus*, and differs much in its properties from the yellow modification, especially in its inflammability, as it does not take fire in the air until heated to above 260°, when it becomes reconverted into the ordinary form, and burns with the formation of phosphorus pentoxide. The specific gravity of amorphous phosphorus is 2·11. The sudden conversion of yellow into red phosphorus can be shown by heating a small piece of ordinary phosphorus in a dry tube with a mere trace of iodine; combination at once occurs, a small trace of volatile phosphorus iodide is formed, and the remainder of the phosphorus is converted into the red modification. The red or amorphous modification of phosphorus can also be obtained in a *crystallized* form by heating red phosphorus in a tube with metallic lead. The phosphorus dissolves in the melted lead, and on cooling separates out in crystals, which possess a bright black metallic lustre, and have a specific gravity of 2·34.

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[1] Φῶς, light, and φέρω, I bear: *lucifer*, from *lux*, light, and *fero*, I bear, is its literal Latin equivalent.

THE OXIDES AND OXY-ACIDS OF PHOSPHORUS.

The only oxide of phosphorus which acts as an acid-forming oxide is the pentoxide, P_2O_5, yielding phosphoric acid. Three other oxides are known—phosphorus oxide, P_4O, and phosphorous oxide, P_4O_6, and phosphorus tetroxide P_2O_4.

Phosphoric acid exists in three modifications:

Orthophosphoric acid,	H_3PO_4	or $PO(OH)_3$.
Metaphosphoric acid,	HPO_3	or $PO_2(OH)$.
Pyrophosphoric acid,	$H_4P_2O_7$	or $P_2O_3(OH)_4$.

Besides these, three other oxy-acids of phosphorus are known, viz.:—

Hypophosphorous acid,	$PH(OH)_2$.
Phosphorous acid,	$P(OH)_3$.
Hypophosphoric acid,	$P_2O_2(OH)_4$.

Phosphorus Oxide, Symbol P_4O, is a yellow powder, formed by heating phosphorus oxychloride (p. 152) with metallic zinc.

Phosphorous Oxide, P_4O_6:—This oxide is formed together with P_4O and P_2O_4 when phosphorus is burnt in a limited supply of air. It crystallizes in thin monosymmetric prisms, melts at 22°·5, and only dissolves very slowly in water, forming phosphorous acid. It oxidizes spontaneously to phosphorus pentoxide on exposure to air or oxygen, and when heated to 50 – 60° it catches fire, burning with an exceedingly brilliant flame.

Phosphorous Acid, or *Hydrogen Phosphite*, *Symbol* H_3PO_3.—This acid is formed when phosphorus is allowed gradually to oxidize in moist air, and also when phosphorus trichloride acts upon water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

By boiling this solution the hydrochloric acid is driven off, and, on cooling, crystals of phosphorous acid are deposited. There are two classes of metallic phosphites: the one contains those which correspond to phosphorous acid, in which two atoms of hydrogen have been replaced by metal; and the second those in which one atom only of hydrogen has been thus replaced: the general forms of the two will therefore be M_2HPO_3 and MH_2PO_3, the letter M denoting an atom of a monovalent metal.

Phosphorus Tetroxide P_2O_4 is formed from the products obtained by burning phosphorus in a limited supply of air, by heating it in a sealed tube at 290°. It forms a crystalline sublimate, which is exceedingly hygroscopic, and dissolves in water with evolution of heat and formation of phosphorous and phosphoric acids.

Phosphorus Pentoxide, or *Phosphoric Anhydride.*

Symbol P_2O_5, *Molecular Weight* 141·72.—This substance is formed when phosphorus burns brightly in excess of air or oxygen. It is a white amorphous light powder, which absorbs moisture with the utmost avidity, forming hydrogen phosphate or phosphoric acid, H_3PO_4: it is for this reason frequently used in the laboratory for the purpose of drying gases. Phosphorus pentoxide is volatile, and may be sublimed unchanged by heating in a test-tube. It can be best prepared by burning small pieces of phosphorus placed one by one in a cup hung in the centre of a large dry glass globe, and blowing in a sufficient supply of dry air by means of a bellows or aspirator. The white powder falls down, and may be shaken out of the globe when the operation is completed.

Trihydrogen Phosphate (Tribasic Phosphoric Acid).

Symbol H_3PO_4, *Molecular Weight* 97·8.—When the preceding compound is brought into contact with water, great heat is evolved, and combination takes place with a hissing noise. If the solution be boiled trihydrogen phosphate is found in solution, being formed thus:

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

Trihydrogen phosphate is also formed when phosphorus is heated with nitric acid: the lower oxides of nitrogen are given off as red fumes, and the phosphorus gradually disappears; by evaporating, and boiling the colourless liquid, trihydrogen phosphate may be obtained. The corresponding calcium salt, $Ca_3(PO_4)_2$, occurring in bone-ash and in many minerals, constitutes the main source of all the phosphorus compounds. If bone-ash be frequently treated with sulphuric acid and the solution evaporated, gypsum gradually separates out, leaving a solution from which hydrogen phosphate can be obtained by neutralizing with ammonium carbonate, filtering, evaporating to dryness the clear liquid thus obtained, and igniting the residue.

If sodium carbonate be added to a solution of trihydrogen phosphate, effervescence will at once ensue from the liberation of carbonic acid, and if the carbonate be added until the solution ceases to redden litmus paper, a salt will be obtained on evaporation which crystallizes in large transparent prisms. This is *rhombic* or *common neutral sodium phosphate;* its composition is represented by the symbol Na_2HPO_4, with twelve molecules of water of crystallization. If caustic soda be added to a solution of this common phosphate, a salt termed the *subphosphate* crystallizes out in small needles on evaporation; the composition of this salt is Na_3PO_4, with twelve atoms of water of crystallization. And if phosphoric acid be added to a solution of common phosphate, the so-called *sodium superphosphate* is formed, NaH_2PO_4; we have therefore the following tribasic hydrogen- and sodium-phosphates:

Trihydrogen Phosphate	H_3PO_4.
Dihydrogen Sodium Phosphate . .	$H_2NaPO_4 + H_2O$.
Hydrogen Di-Sodium Phosphate . .	$HNa_2PO_4 + 12H_2O$.
Tri-Sodium Phosphate	$Na_3PO_4 + 12H_2O$.

The three atoms of hydrogen in trihydrogen phosphate may be replaced by three different metals; thus *microcosmic salt* is hydrogen sodium ammonium phosphate, $HNaNH_4PO_4 + 4H_2O$.

All these substances are distinguished by giving a *yellow* precipitate with solution of silver nitrate, consisting of trisilver phosphate, Ag_3PO_4; and by producing with ammonia and magnesium sulphate, a white crystalline precipitate of ammonium magnesium phosphate, $NH_4MgPO_4+6H_2O$.

Small traces of phosphates may readily be detected by the yellow precipitate which forms on addition of a nitric acid solution of ammonium molybdate.

Pyrophosphoric Acid, or *Hydrogen Pyrophosphate*.

Symbol $H_4P_2O_7$.—If tribasic phosphoric acid be heated for some time to 210°, a crystalline mass of pyrophosphoric acid is formed and water is liberated:

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

This acid is tetrabasic, the four atoms of hydrogen being replaceable, either all or in part, by metals : thus, if common sodium phosphate be heated to redness, water is driven off, *sodium pyrophosphate*, $Na_4P_2O_7$, remains, two molecules of neutral phosphate yielding one of pyrophosphate :

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7.$$

When this salt is dissolved in water, it can be re-crystallized, and does not take up water again so as to pass back to the state of common phosphate (except on long-continued boiling of its solution). This substance gives with silver nitrate a *white* precipitate of silver pyrophosphate, $Ag_4P_2O_7$: and thus this class of phosphates may be distinguished from the preceding or tribasic phosphates. A so-called acid sodium pyrophosphate, having the composition $Na_2H_2P_2O_7$, is also known.

Metaphosphoric Acid, or *Monohydrogen Phosphate*.

Symbol HPO_3, is obtained in the form of a transparent ice-like mass by evaporating the solution of trihydrogen phosphate and igniting the residue. On dissolving this glacial acid in cold water, a solution of monohydrogen phosphate is obtained; but this, on boiling, changes to the trihydrogen phosphate.

If microcosmic salt, $Na(NH_4)HPO_4+4H_2O$, is heated, water and ammonia are driven off, and *sodium metaphosphate*, $NaPO_3$, is left: this dissolves unaltered in water, forming one of a third class of phosphates termed *monobasic phosphates*, or *metaphosphates*. The solutions of these salts may be distinguished from those of the two preceding classes of salts by their producing with solutions of salts of calcium and of silver gelatinous precipitates consisting of the metaphosphates of these metals.

From the above it is seen that three modifications of phosphoric acid are known, or, rather, three different acids, each giving rise to a class of metallic salts. Thus we have—

(1) Trihydrogen phosphate, or phosphoric acid, H_3PO_4, and trisodium phosphate, Na_3PO_4.

(2) Tetrahydrogen phosphate, or pyrophosphoric acid, $H_4P_2O_7$, and sodium pyrophosphate, $Na_4P_2O_7$.

(3) Monohydrogen phosphate, or metaphosphoric acid, HPO_3, and sodium metaphosphate, $NaPO_3$.

Each of the above hydrogen phosphates can be prepared by passing sulphuretted hydrogen through water containing in suspension the corresponding silver salts:

$$(1)\ 2Ag_3PO_4 + 3H_2S = 2H_3PO_4 + 3Ag_2S.$$
$$(2)\ Ag_4P_2O_7 + 2H_2S = H_4P_2O_7 + 2Ag_2S.$$
$$(3)\ 2AgPO_3 + H_2S = 2HPO_3 + Ag_2S.$$

Hypophosphorous Acid.

Symbol H_3PO_2.—In addition to the phosphates and phosphites, a class of salts termed Hypophosphites is also known. The composition of *hydrogen hypophosphite* is represented by the formula HPH_2O_2, and that of sodium hypophosphite by $NaPH_2O_2$; and these salts may be supposed to be hydrogen or sodium metaphosphate, HPO_3 and $NaPO_3$, in which one atom of oxygen has been replaced by its equivalent, or two atoms, of hydrogen. Sodium hypophosphite is obtained by acting with caustic soda on phosphorus, when phosphuretted hydrogen gas is evolved, and a solution of sodium hypophosphite remains behind.

Hypophosphoric Acid, $H_4P_2O_6$.

An acid having the above composition is also known. It is contained, together with phosphorus and phosphoric acids, in the acid syrupy liquid formed when sticks of phosphorus partly covered with water are exposed to the air. It can be easily isolated, as it forms a sparingly soluble hydrogen sodium salt, $H_2Na_2P_2O_6$. Its constitution is similar to that of pyrophosphoric acid, as is shown in the following formulæ :

Phosphorous Acid.	Orthophosphoric Acid.
$P(OH)_3$.	$PO(OH)_3$.
Hypophosphoric Acid.	Pyrophosphoric Acid.
$O\left\{\begin{matrix}P(OH)_2\\PO(OH)_2\end{matrix}\right.$.	$O\left\{\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix}\right.$.

PHOSPHORUS AND HYDROGEN.

Three compounds of phosphorus and hydrogen are known PH_3, a gas ; P_2H_4, a liquid ; P_4H_2, a solid substance.

Phosphuretted Hydrogen, or *Phosphine*.

Symbol PH_3, *Molecular Weight* 33·96, *Density* 16·98.—This gas is obtained in the pure state by the decomposition of hydrogen phosphite :

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

or of the iodide of phosphonium, PH_4I. But it is generally prepared by the action of caustic potash on phosphorus :

$$3KOH + P_4 + 3H_2O = 3KPH_2O_2 + PH_3 ;$$

potassium hypophosphite being formed. It is a colourless gas, smelling like putrid fish.

Each bubble of the gas prepared by the last method takes fire spontaneously on coming in contact with the air, forming singular rings of phosphorus pentoxide, which expand as they rise. This self-inflammability of the gas depends upon the presence of small quantities of the liquid hydride P_2H_4, which may be condensed to a volatile and very inflammable liquid by passing the gaseous hydride through a tube cooled by a freezing mixture.

PHOSPHORUS AND CHLORINE.

Two chlorides of phosphorus are known—*phosphorus trichloride*, PCl_3, and *phosphorus pentachloride*, PCl_5. The first of these is a colourless strongly-fuming liquid, which is easily formed by passing a current of chlorine gas over phosphorus contained in a retort: when thrown into water, it sinks down as a heavy oil, but is gradually decomposed, hydrogen phosphite and hydrochloric acid being formed. The specific gravity of the trichloride is 1·61, and its boiling-point is 76°. Phosphorus trichloride rapidly absorbs chlorine gas and is converted into the pentachloride, a yellowish solid substance, which is also formed when phosphorus is burnt in an excess of chlorine.

Phosphorus pentachloride is decomposed in presence of excess of water, forming trihydrogen phosphate and hydrochloric acid; but when only a limited quantity of water is present, a liquid termed *phosphorus oxychloride* is formed, having the composition $POCl_3$, and boiling at $107^{\circ}\cdot2$; thus:

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

The oxychloride can also be obtained perfectly pure, by heating the pentachloride with the pentoxide; thus:

$$3PCl_5 + P_2O_5 = 5POCl_3.$$

These compounds are much used in chemical research, for introducing chlorine into other combinations.

Corresponding compounds of phosphorus with bromine and iodine are also known, and resemble the chlorine derivatives. *Phosphorus pentafluoride*, PF_5, obtained by the action of phosphorus pentachloride on arsenic trifluoride according to the equation

$$3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$$

is a non-inflammable gas.

With sulphur phosphorus forms several compounds: and it is an interesting fact that two of these compounds, P_2S_3, and P_2S_5 correspond in composition with the oxides P_2O_3 and P_2O_5. The oxide corresponding to P_2S, however, is as yet unknown.

LESSON XVI

ARSENIC

Symbol As, *Atomic Weight* 74·9, *Density of Vapour* 149·8.[1]—Arsenic closely resembles phosphorus in its chemical properties and in those of its compounds, although in its physical characters, such as specific gravity, lustre, &c., it bears a greater analogy to the metals: indeed, it may be considered the connecting link between these two divisions of the elements, antimony and bismuth being closely connected with it on the one hand, and phosphorus and nitrogen on the other. Arsenic is sometimes found in the free state, but more frequently combined, chiefly with iron, nickel, cobalt, and sulphur. It is also contained in very small quantities in many mineral springs. In order to separate arsenic from any of the metallic ores in which it occurs, the ore is roasted, *i.e.* exposed to a current of heated air in a reverberatory furnace; the arsenic combines with the atmospheric oxygen, forming *arsenic trioxide*, As_2O_3, which is carried in the state of vapour from the furnace into long chambers or flues in which the trioxide (commonly known as arsenious acid, or white arsenic) is deposited. Metallic arsenic may be prepared from this oxide by mixing it with charcoal and sodium carbonate, and heating in a closed crucible, the upper part of which is kept cool: arsenic condenses in the cool part of this apparatus as a solid with a brilliant greyish lustre. It tarnishes in the air from oxidation; it has a specific gravity of 5·7; and when heated to dull redness, volatilizes as a colourless vapour without undergoing fusion, the vapour possessing a remarkable garlic-like smell. Arsenic when heated in the air takes fire, and burns with a bluish flame, forming arsenic trioxide, As_2O_3; when thrown into chlorine, it instantly takes fire, forming arsenic trichloride, $AsCl_3$.

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[1] The volume occupied by an atom of (gaseous) arsenic weighing 74·9 is only half of that occupied by the other elements generally: in this respect arsenic resembles phosphorus.

OXIDES OF ARSENIC.

Two compounds of arsenic and oxygen are known, (1) *Arsenic Trioxide*, As_4O_6; (2) *Arsenic Pentoxide*, As_2O_5.

Arsenic Trioxide.—Symbol As_4O_6, *Molecular Weight* 395·6, *Density of Vapour* 197·7.—This substance (commonly called arsenious acid or white arsenic) is formed when arsenic is burnt in the air or in oxygen, but it is generally prepared by roasting arsenical pyrites, FeSAs; its specific gravity is 3·7. It exists in two distinct forms, the crystalline and the vitreous: it occurs in the first modification crystallized in brilliant octahedra, and in the second as a semi-transparent glass-like solid, devoid of crystalline structure: this form of the substance, on standing, becomes opaque like porcelain, diminishing in specific gravity. Arsenic trioxide is slightly soluble in water: the solution (which may be considered to contain true arsenious acid or trihydrogen arsenite, H_3AsO_3, analogous to phosphorous acid) has a feebly acid reaction. It dissolves more readily in hydrochloric acid, and is freely soluble in solutions of the alkalis, arsenites of the general form M_3AsO_3 being formed: thus, tri-silver arsenite is Ag_3AsO_3. The alkaline arsenites are soluble in water; those of the metals of the alkaline earths and heavy metals are insoluble in water. Sodium arsenite is used largely in calico-printing; Scheele's green and emerald green are compounds containing arsenic trioxide and copper, both of which are made in large quantities for employment as pigments. All the soluble arsenites are dreadfully poisonous; the best antidote is freshly-prepared ferric hydrate (hydrated ferric oxide), or magnesia, which form insoluble arsenites, and thus prevent the poison from entering into the system. When heated to about 220° C. arsenic trioxide volatilizes without melting, forming an inodorous and colourless vapour. It is occasionally met with crystallized in long needles of the same form as the crystals of the corresponding oxide of antimony (see p. 257).

Arsenic Pentoxide.—Symbol As_2O_5, *Molecular Weight* 229·6. —This oxide (commonly called arsenic acid) is obtained by acting upon the trioxide with nitric acid, evaporating to dryness, and heating to a temperature of 270°. It forms a non-crystalline white powder, which, when strongly heated, decomposes into As_2O_3, and O_2. This powder is dissolved by water, and the solution yields crystals of arsenic acid, or trihydrogen arsenate, H_3AsO_4: the metallic compounds corresponding to this are called arsenates, and resemble the corresponding tribasic phosphates (p. 148) in composition, whilst they are identical with them in crystalline form. Thus we have—

Trisodium Arsenate	$Na_3AsO_4 + 12H_2O$.
Hydrogen Di-sodium Arsenate .	$HNa_2AsO_4 + 12H_2O$.
Dihydrogen Sodium Arsenate . .	$H_2NaAsO_4 + H_2O$.
Trihydrogen Arsenate	H_3AsO_4.

With mixed solutions of a magnesium and an ammonium salt, soluble arsenates, like phosphates, form an insoluble precipitate, having the composition $NH_4MgAsO_4 + 6\ H_2O$ (ammonium magnesium arsenate). The arsenates of the alkali-metals are soluble, those of the other metals insoluble, in water. Tri-silver arsen*ate* is a characteristic salt of a brownish-red colour, whereas tri-silver arsen*ite* has a bright yellow tint. Arsenic acid acts as a poison, but it is less powerful than arsenious acid.

No arsenates corresponding to the pyro- and meta-phosphates have been, as yet, obtained : compounds having the composition $Na_4As_2O_7$ and $NaAsO_3$ have indeed been prepared by heating a tribasic salt ; but on solution in water they combine again with it, and then present only the characteristics of the tribasic acid.

ARSENIC AND HYDROGEN.

Arseniuretted Hydrogen, or *Arsine.—Symbol* AsH_3, *Combining Weight* 77·9, *Density* 38·9. This compound, which corresponds to phosphuretted hydrogen, and to ammonia, is formed by decomposing an alloy of arsenic and zinc with sulphuric acid. It is a colourless gas, possessing a fœtid odour of garlic, and acts as a most deadly poison, the discoverer, Gehlen, having been killed by inhaling a single bubble of the pure gas. When cooled to −40°, it condenses to a colourless liquid. Arseniuretted hydrogen burns with a bluish flame, and deposits arsenic upon a cold body held in the flame: below a red heat it is decomposed into arsenic and hydrogen.

ARSENIC AND THE HALOGENS.

Arsenic unites with chlorine, bromine, and iodine, to form *arsenic trichloride*, *tribromide*, and *tri-iodide*. The trichloride is a colourless volatile liquid, boiling at 134°, which decomposes in contact with water, yielding arsenious and hydrochloric acids.

ARSENIC AND SULPHUR.

Three sulphides of arsenic are known—Arsenic Disulphide, As_2S_2, which occurs naturally as *Realgar*; Trisulphide, As_2S_3, also occurring in nature as *Orpiment*; and Pentasulphide, As_2S_5. Orpiment may be obtained by passing a stream of sulphuretted hydrogen gas through the acid solution of the corresponding oxide, when it is precipitated as a yellow powder. The arsenic sulphides form with the sulphides of the alkali-metals compounds bearing the same analogy to the trisulphide and pentasulphide that arsenites and arsenates do to the trioxide and pentoxide: in short, these compounds are *sulphur salts*, the arsenites and arsenates being *oxysalts*; hence they are called *sulph*arsenites and *sulph*arsenates, thus:

$$As_2S_3 + 3K_2S = 2K_3AsS_3,$$
$$As_2O_3 + 3K_2O = 2K_3AsO_3.$$

Detection of Arsenic.

Arsenic possesses characters of so peculiar a kind, that its presence even in very minute traces can be detected with certainty. From its solutions it can be precipitated as sulphide, by the aid of sulphuretted hydrogen: and this sulphide, when dried and fused in a small test tube with a mixture of potassium cyanide and sodium carbonate, yields a ring of metallic arsenic : on heating, the metal is oxidized to the trioxide, which deposits in minute octahedral crystals. These, when boiled with water, yield a solution giving a bright green precipitate with neutral copper solutions, and a bright yellow one with neutral silver salts. Arsenic in solution may be also detected by the evolution of arseniuretted hydrogen, on adding zinc and sulphuric acid to the solution to be tested : on burning the gas, arsenic is deposited in the metallic state upon a piece of cold porcelain held in the flame (Marsh's test). This mirror dissolves in solution of sodium hypochlorite ; and if treated with nitric acid, and the solution neutralized, yields with silver nitrate solution a red precipitate of tri-silver arsenate. Many compounds of arsenic heated on charcoal in the inner blowpipe flame give a garlic odour of arsenic. Solutions containing arsenic when boiled with hydrochloric acid and clean copper, deposit a coating of arsenic upon the copper : this coating, on drying and heating in a test-tube, gives a ring of mirror arsenic, which may be oxidized to trioxide and tested as before (Reinsch's test). By these and other reactions, the presence of the minutest portion of arsenic may be detected with certainty. Great care must, however, be taken to ensure the absence, in such toxicological experiments, of every trace of arsenic in the reagents used.

The general chemical analogy between nitrogen, phosphorus, and arsenic is well seen when their corresponding compounds are examined : thus the hydrides, oxides, and chlorides have an analogous composition.

$$\begin{array}{cccc} N_2O_3 & N_2O_5 & NH_3 & NCl_3 \\ P_2O_3 & P_2O_5 & PH_3 & PCl_3 \\ As_2O_3 & As_2O_5. & AsH_3. & AsCl_3. \end{array}$$

These three elements are all *trivalent* or *pentavalent;* that is, one atom of each of these bodies is equivalent to, and capable of replacing, three or five atoms of hydrogen. Antimony and bismuth (see pp. 256 and 258) exhibit in their chemical relations a striking resemblance to the foregoing group.

LESSON XVII

ATOMS AND MOLECULES

In the foregoing pages we have seen that all chemical processes take place according to simple unalterable laws. One of these laws tells us that the elements unite together to form compounds in proportions indicated by their combining weights or in simple multiples of these weights. In order to explain this fact we assume that all matter is made up of very small particles which are chemically indivisible and which are termed *Atoms*, and the atom of each elementary substance differs essentially from that of every other. All the atoms of each element are alike, and chemical compounds are formed by the approximation of unlike atoms. Hence the smallest particles of a compound consist of a group of atoms; this group, which can be divided by chemical but not by mechanical means, is termed a *Molecule*.

The smallest particle of an element in the free state (that is to say when the element is isolated and exists apart from other elements) is, however, not necessarily a single atom, but a group of atoms (in most cases two) mechanically indivisible, or a molecule. This explains (see also p. 99) why elementary bodies act more energetically and enter more readily into combination at the moment of their liberation from a combination (in the *nascent state*) than when in the free state.

When chemical changes occur, it is the molecules which react upon one another, and the change, interchange, or elimination consists in the alteration of position of certain atoms contained in the groups. When an element is set free from a compound the liberated atoms join together to form molecules, unless some body is present with which the element can combine. It has already been pointed out (pp. 57 and 58) that *equal volumes of all the different gases, both elementary and compound, contain the same number of particles or integrant molecules* (Avogadro).[1] This explains the well-known fact that all gaseous bodies obey the same law of expansion by heat, and of alteration of volume by alteration of pressure.

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[1] It is not strictly correct to assume that each single atom of one element occupies the same space as each single atom of another element, or that the single molecule of a simple compound occupies the same space as the single molecule of a more complicated compound, for interspaces doubtless exist *between* the atoms and between the molecules.

In order to obtain the molecular weight of any body which is volatile without decomposition, all we have to do is to determine how many times the gas is heavier than hydrogen, and to multiply this number by 2.

	Density of the Gas or Vapour.	Molecular Weight.	Atomic Weight.
Hydrogen	1	2	1
Chlorine	35·37	70·74	35·37
Phosphorus	61·92	123·84	30·96
Arsenic	149·8	299·6	74·9
Mercury	99·9	199·8	199·8.

If we divide this molecular weight by the atomic weight we obtain the number of atoms contained in the molecule. The molecules of hydrogen, chlorine, and most of the other elements known in the gaseous state contain 2 atoms. Phosphorus and arsenic, however, contain 4 atoms in the molecule, whilst the molecular weight of mercury and of some other volatile metals is the same as the atomic weight, or the molecule of these elements contains only one atom.

By an *atom*, we therefore understand the smallest portion of a chemical element which can enter into a chemical compound.

By a *molecule*, the smallest portion of a simple or compound body which can occur in the free state or which can take part in a chemical reaction. If we wish fully to represent the alterations which occur when a chemical change goes on we must employ *molecular formulæ*, but for the sake of simplicity we frequently use *atomic formulæ*.

Thus if we write $KClO_3 = KCl + O_3$ we signify that potassium chlorate splits up into potassium chloride and oxygen; we know, however, that this decomposition takes place in two stages:

(1) $2KClO_3 = KCl + KClO_4 + O_2$.
(2) $KClO_4 = KCl + 2O_2$.

And we see that in this case not less than one molecule of any element or compound takes place in the reaction.

We can now explain why oxide of silver and hydrogen dioxide when brought together yield free oxygen gas (see p. 46).

$$\left.\begin{matrix}\mathrm{Ag}\\\mathrm{Ag}\end{matrix}\right\}\mathrm{O} + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}_2 = \left.\begin{matrix}\mathrm{Ag}\\\mathrm{Ag}\end{matrix}\right\} + \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O} + \left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}$$

Silver unites but feebly with oxygen, and oxide of silver is easily decomposed on heating; in the same way in hydrogen dioxide, the second atom of oxygen is only feebly held in combination, and when the compounds are brought together the two separate atoms of oxygen from each compound unite forming a molecule of oxygen, the separate atoms having a stronger attraction for one another than for the substances with which they are respectively combined. A similar explanation may be given of the action of ozone on hydrogen dioxide (p. 46); the molecule of ozone contains 3 atoms of oxygen, one of which is readily separated, and this combines with the loosely attached atom of oxygen contained in the molecule of hydrogen dioxide:

Ozone.		Hydrogen dioxide.		Water.		Free oxygen.
$\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}\mathrm{O}$	+	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}_2$	=	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$	+	$2\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}$.

Quantivalence or *Valency of the Elements.*

If we compare together the compounds of the preceding elements with hydrogen, we find that these exhibit a distinct difference in combining power. The first group embraces compounds, of which the molecule contains one atom of hydrogen combined with one atom of the element. In the second, the atom of each element is combined with 2 of hydrogen; in the third, 3 atoms of hydrogen are present; whilst the fourth group contains 4 atoms of hydrogen in the molecule.

	Hydrogen.	Hydrochloric Acid.	Hydrobromic Acid.	Hydriodic Acid.	Hydrofluoric Acid.
(1)	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{Br}\end{matrix}\right\}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{I}\end{matrix}\right\}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{F}\end{matrix}\right\}$

	Water.	Hydrogen Sulphide.	Hydrogen Selenide.	Hydrogen Telluride.
(2)	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{S}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{Se}$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{Te}$.

	Ammonia.	Phosphine.	Arsine.
(3)	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{N}.$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{P}.$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{As}.$

	Methane.	Silicon Hydride.
(4)	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{C}.$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{Si}.$

The same relations are equally well marked in the compounds of these elements with chlorine, or with any other element of the first group.

	Chlorine Monoxide.	Hypochlorous Acid.	Hypobromous Acid.
(1)	$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{O}.$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{O}.$	$\left.\begin{matrix}\mathrm{H}\\\mathrm{Br}\end{matrix}\right\}\mathrm{O}.$
	Phosphorus Trichloride.	Arsenic Trichloride.	Arsenic Tri-iodide.
(2)	$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{P}.$	$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{As}.$	$\left.\begin{matrix}\mathrm{I}\\\mathrm{I}\\\mathrm{I}\end{matrix}\right\}\mathrm{As}.$
	Carbon Tetrachloride.	Methyl Chloride.	Silicon Tetrachloride.
(3)	$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{C}.$	$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{C}.$	$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{Si}.$

Hence it is clear that we can divide the elements into certain groups. The elements of the first group combine atom for atom with hydrogen, they are *monovalent* elements or monads, and they possess only one combining unit. The members of the second group are *divalent*, or may be termed *dyads*, each atom possessing two combining units and requiring two monad atoms for saturation. The elements of the nitrogen group and boron are *trivalent*, or form the *triad* class; whilst carbon and silicon are *tetravalent*, or are termed *tetrads*. This difference of combining power is termed *Quantivalence* or *Valency* of the elements. The elements belonging to one class are *equivalent*, and each one can replace the other in equal proportions. One atom of a dyad is equivalent to 2 atoms of a monad, and one of a triad to 3 of a monad; and again 3 of a dyad are equivalent to 2 of a triad, &c. The following equations illustrate this quantivalence.

$$\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}\mathrm{O} + 2\left.\begin{matrix}\mathrm{H}\\\mathrm{Cl}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O} + 2\left.\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right\}.$$

$$3\mathrm{S}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right. + 2\mathrm{As}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\end{matrix}\right. = 6\mathrm{HCl} + \mathrm{As}_2\left\{\begin{matrix}\mathrm{S}\\\mathrm{S}\\\mathrm{S}.\end{matrix}\right.$$

$$\mathrm{C}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right. + 2\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\} = \mathrm{C}\left\{\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right. + 2\mathrm{O}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}.\end{matrix}\right.$$

In like manner the *metallic* elements can be divided into classes according to their valency, their power of combining with chlorine being taken as a measure of their quantivalence, few compounds of metals with hydrogen being known, thus :

Potassium Chloride $\left.\begin{matrix}\mathrm{K}\\\mathrm{Cl}\end{matrix}\right\{$ Calcium Chloride $\mathrm{Ca}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}.\end{matrix}\right.$

Antimony Trichloride $\mathrm{Sb}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}.\end{matrix}\right.$ Tin Tetrachloride $\mathrm{Sn}\left\{\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}\\\mathrm{Cl}.\end{matrix}\right.$

The monad elements unite amongst themselves to form only few and simple compounds ; but if an element possessing more than one combining unit enter into combination, the number of possible compounds becomes larger. Chlorine and hydrogen form only one compound ; in the case of oxygen and hydrogen on the other hand we are acquainted with two compounds. In hydrochloric acid the two single combining units of the two atoms are saturated by mutual attachment ; if one atom of monad hydrogen attach itself to one of dyad oxygen, one of the combining units of the oxygen atom is left unsaturated, and this may either combine with hydrogen to form water H—O—H, or another atom of oxygen may be attached, and this again may saturate itself with hydrogen, and we obtain hydrogen dioxide H—O—O—H.

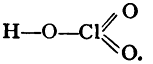
Variation of Valency.

One and the same element may, however, possess a *different* quantivalence in different compounds. Thus it would appear that chlorine is a monad in hypochlorous acid, a triad in chlorous acid, a pentad in chloric acid, and a heptad in perchloric acid. This is rendered evident by the following graphic formulæ :

Hypochlorous Acid, $\mathrm{H{—}O{—}Cl}$.

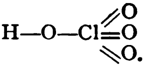
Chlorous Acid, $\mathrm{H{—}O{—}Cl{=}O}$.

Chloric Acid,



$$\mathrm{H{—}O{—}Cl}\begin{array}{l} \diagup\!\!\!\!\diagup \mathrm{O} \\ \diagdown\!\!\!\!\diagdown \mathrm{O.} \end{array}$$

Perchloric Acid,



$$\mathrm{H{—}O{—}Cl}\begin{array}{l} \diagup\!\!\!\!\diagup \mathrm{O} \\ = \mathrm{O} \\ \diagdown\!\!\!\!\diagdown \mathrm{O.} \end{array}$$

Similarly sulphur selenium and tellurium are both tetrads and hexads; and the members of the nitrogen group both triads and pentads. Only one compound of carbon is, on the other hand, known in which this element does not act as a tetrad, and this is carbon monoxide, in which carbon appears to act as a dyad. The pentavalent character of the elements of the nitrogen group is clearly seen in such cases as the direct combination of ammonia and hydrochloric acid to form ammonium chloride :

$$NH_3 + HCl = NH_4Cl.$$

Then again, phosphorus trichloride absorbs two atoms of chlorine, and is converted into the pentachloride

$$PCl_3 + Cl_2 = PCl_5.$$

These compounds, however, with the single exception of phosphorus pentafluoride PF_5, only exist in the solid or liquid state; when they are heated they decompose into the two molecules from which they have been formed. In some cases this decomposition can be readily seen; silver chloride absorbs ammonia in the cold and forms the compound $AgCl.2NH_3$, but this compound when heated decomposes into chloride of silver and gaseous ammonia. Other compounds, such as pentachloride of phosphorus, appear to volatilize without decomposition, but in this case it can be proved that the vapour is a mixture and contains the molecules of two gases, phosphorus trichloride and free chlorine. The vapour densities of these bodies, accordingly, do not obey the usual law; thus the vapour of chloride of ammonium, if it consisted of similar molecules, must possess the density of 26·69. In fact, however, its density if measured at the ordinary pressure is only the half of this number, for four volumes contain 1 molecule of ammonia and 1 of hydrochloric acid; hence its density (or the weight of one volume) is $\frac{36{\cdot}37+17{\cdot}01}{4}=13{\cdot}34$.

Compound Radicals.

Not only then can the *elements* be considered as possessing varying quantivalence, but also those groups of elementary atoms which act collectively as elements and to which the name of *compound radicals* is given. These radicals contain dyad, triad, or tetrad elements, whose combining units are not completely saturated. Thus nitric acid may be considered as water, in which one atom of hydrogen is replaced by the group NO_2, termed *nitroxyl.*

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O \quad \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O.$$

This is a monad radical, for 2 atoms of oxygen only possess 4 combining units, and hence one of the five combining units of the nitrogen atom remains free or unsaturated, and the group NO_2 can take the place of a monad element. In like manner the constitution of all the oxy-acids and also the hydroxides can be represented. These compounds contain the group OH (water minus 1 atom of hydrogen); this group may be considered as a monad radical, and has received the name of *Hydroxyl.* That this radical plays the part of a monad element such as chlorine is seen in the following equations:

$$2HCl + Na_2 = H_2 + 2NaCl.$$
$$2HOH + Na_2 = H_2 + 2NaOH.$$

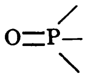
The dyad radical carbonyl $=C=O$ is contained in the following compounds:

Carbonyl Chloride.	Carbonyl Sulphide.	Sodium Carbonate.	Sodium Bicarbonate.
$CO\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	$CO:S$	$CO\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.$	$CO\left\{\begin{matrix}OH\\ONa.\end{matrix}\right.$

The radical sulphuryl $SO_2=$ is a dyad radical, and gives rise to the following compounds :

Sulphuric Acid.	Chlorosulphonic Acid.	Sulphuryl Chloride.	Nitro-Sulphonic Acid.
$SO_2\left\{\begin{matrix}OH\\OH\end{matrix}\right.$	$SO_2\left\{\begin{matrix}OH\\Cl\end{matrix}\right.$	$SO_2\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	$SO_2\left\{\begin{matrix}OH\\NO_2.\end{matrix}\right.$

Acid Potassium Sulphate.	Potassium Sulphate.	Sulphur Trioxide.
$SO_2\left\{\begin{matrix}OK\\OH\end{matrix}\right.$	$SO_2\left\{\begin{matrix}OK\\OK\end{matrix}\right.$	$SO_2\{O.$

Again in the oxy-acids of phosphorus the *triad radical* PO having probably the following constitution  yields

Phosphoryl Chloride.	Orthophosphoric Acid.	Metaphosphoric Acid.
$PO\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.$	$PO\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$	$PO\left\{\begin{matrix}OH\\O\end{matrix}\right.$

Pyrophosphoric Acid.	Hypophosphoric Acid.	Phosphorus Pentoxide.
$O\left\{\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix}\right.$	$O\left\{\begin{matrix}P(OH)_2\\PO(OH)_2\end{matrix}\right.$	$O\left\{\begin{matrix}PO.O\\PO.O\end{matrix}\right.$

The quantivalence of an element, or of a compound radical, may be conveniently expressed by placing the Roman numerals above the symbol of those which are not monads, thus :

$$H,\ \overset{II}{O},\ \overset{III}{N},\ \overset{IV}{C},\ NO_2,\ \overset{II}{SO_2},\ \overset{III}{PO},\ \&c.$$

LESSON XVIII

THE METALLIC ELEMENTS

THE metals are much more numerous than the non-metallic elements ; there are at least fifty-three of the former, and fifteen of the latter. Very many metals are, however, found in small quantities, and the properties of some of these and their compounds are but little known; so that in this work we shall only consider the most important and commonly occurring metals.[1]

It has already been stated that the division of the elements into these two classes is one of convenience only, and is not founded on any essential difference: thus arsenic and antimony may, in some respects, be considered as metals, and in others as non-metals.

All metals, with the single exception of mercury (a liquid), are solid at the ordinary temperature; they possess a high power of reflecting light, causing the bright glittering appearance known as the *metallic lustre;* they are opaque, except in the thinnest possible films, when, as in the case of gold leaf, they allow light to pass; they are better conductors of heat and electricity than the non-metals, and, as a rule, they have higher specific gravities than these. The metals differ widely from each other, both in their physical and chemical properties, and are, accordingly, adapted for different uses: those metals which are lightest exhibit in general the greatest power of union with oxygen, whilst the heavier metals undergo oxidation with difficulty.

SPECIFIC HEAT AND ATOMIC HEAT.

When equal weights of different bodies are raised through the same number of degrees of temperature, they take up different amounts of heat; or different bodies possess different *capacities for heat.* Thus the amount of heat needed to raise a kilogram of water through 100° C. is 31 times as large as that required to raise the same weight of platinum through the same interval of temperature, or in other words, the same amount of heat that raises one kilo. of water through 100° will raise 31 kilos. of platinum through the same temperature. Hence the *specific heat* of platinum is said to be $\frac{1}{31}$, or 0·032; that of water being taken as the unit. The specific heat of the same substance is different according as the substance is solid, liquid, or gaseous; but the specific heats of the metals in the solid state exhibit a remarkable relation to their atomic weights. It has been found that if instead of calculating the specific heats for *equal* weights, we take the *atomic* weights of the metals, the numbers expressing the capacity for heat of the atoms are all equal; *or the metals all possess the same atomic heat.* This is clearly seen if we multiply the specific heats of the metals by the corresponding atomic weights; thus:

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[1] See footnote, p. 8.

	Specific Heat.		Atomic Weight.		Atomic Heat.
Lead	0·0315	×	206·4	=	6·5
Platinum	0·0324	×	196·7	=	6·4
Silver	0·0570	×	107·66	=	6·1
Tin	0·0548	×	117·8	=	6·5
Zinc	0·0955	×	64·9	=	6·2

Hence we have in the determination of the specific heat a means of checking the atomic weight of a metal, or of ascertaining it in a doubtful case. Thus, in the case of thallium, a metal discovered in 1861, chemists were in doubt whether it most resembled lead or the alkali metals: if it was to be classed as a dyad with lead, its atomic weight must be 407·2; if it was placed with the monad alkali metals its atomic weight would be $\frac{407{\cdot}2}{2}=203{\cdot}6$. The specific heat of thallium was, however, found to be 0·033: and if we divide this into 6·4, the common atomic heat of the metals, we get the number 194, a number much nearer to 203·6 than to 407·2. The difference here noticed between 194 and 203·6 is due to the great difficulty of accurately determining the specific heat of bodies and the errors which arise from the variation of physical condition.

Another metal, viz. indium, discovered in 1863, was at first believed to be a dyad, as it closely resembled zinc, but as soon as its specific heat had been ascertained to be 0·057 it was clear that the atomic weight of the metal was not 75·6, as it had been assumed to be, but 1·5 times larger, for 113·4 × 0·057 = 6·46. Hence the chloride is $InCl_3$.

The following non-metals have the same atomic heat as the metals: *chlorine*, *bromine*, *iodine*, *selenium*, *tellurium*, *arsenic*.

The atomic heats of such elements as nitrogen and chlorine cannot, it is true, be determined in the solid state, but their atomic heats can be calculated from the molecular heats of their solid compounds, for *the elements in the*

solid state possess the same atomic heats as in their compounds; and hence the molecular heat is the sum of the atomic heats of the combined elements, as is shown in the following list:

	Specific Heat.		Molecular Weight.				
Silver chloride, $AgCl$	0·089	×	143·5	=	2	×	6·4
Sodium chloride, $NaCl$	0·219	×	58·5	=	2	×	6·4
Potassium bromide, KBr . . .	0·107	×	119·1	=	2	×	6·4
Tin di-chloride, $SnCl_2$	0·102	×	189	=	3	×	6·4
Mercuric iodide, HgI_2	0·0423	×	454	=	3	×	6·4
Platinum potassium chloride, K_2PtCl_6	0·118	×	488·6	=	9	×	6·4

The remaining elements have all an atomic heat smaller than 6·4; thus the atomic heats of sulphur, nitrogen, boron, and phosphorus are about 5·4; of fluorine, 5; of silicon, 4·8; of oxygen, 4; of hydrogen, 2·3; and of carbon, 1·8.[1] In the case of these elements the atomic heats are calculated from the molecular heats of their compounds in accordance with the above-mentioned law, as the following examples show:

	Spec. Heat.		Molec. Weight.		Molec. Heat.
Ice, H_2O	0·478	×	18	=	8·6 = 4 + 2 × 2·3.
Mercuric oxide, HgO	0·048	×	216	=	10·4 = 6·4 + 4.
Arsenic trioxide, As_2O_3	0·125	×	198	=	24·8 = 2 × 6·4 + 3 × 4.
Calcium carbonate, $CaCO_3$ . .	0·202	×	100	=	20·2 = 6·4 + 1·8 + 3 × 4.
Potassium sulphate, K_2SO_4 .	0·196	×	174·2	=	34·2 = 2 × 6·4 + 5·4 + 3 × 4.
Carbon hexachloride, C_2Cl_6 . .	1·177	×	237	=	42·0 = 2 × 1·8 + 6 × 6·4.

Occurrence and Distribution of the Metals.

Only a few of the metals occur in the free or uncombined state in nature; in general they are found combined with oxygen, sulphur, or some other non-metal. These metallic compounds exist most variously distributed throughout the earth's crust; some are known to occur in only one or two localities, and even then only in minute quantity, whereas others are found widely distributed in enormous masses. As is seen by reference to the table on p. 8 the metals aluminium, iron, calcium, magnesium, and sodium occur in very large quantities, forming, when united with oxygen and silicon, the whole mass of granitic rocks composing our globe; but it is not from these sources that the metals in question can be obtained for the purposes of the arts. For this object we employ other combinations, found in smaller quantity, from which the metals can be more easily extracted than from the silicates: and these compounds are termed the *metallic ores.*

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[1] The specific heat of carbon has been found to rise quickly with the temperature. At 800° it becomes constant, and the atomic heat is then under these circumstances, 5·5, and therefore closely approaches that of the metals. The same change is noticed in the specific heats of silicon and boron.

The heavy metals and their ores generally occur interspersed throughout the old granitic or early sedimentary rocks in the form of veins or lodes, which are cracks, or fissures, running through the rock in a particular direction, and filled up with a metallic ore. Other ores, such as ironstone, are found amongst the more recent sedimentary formations, having been deposited in large masses, probably from aqueous solution.

The consideration of the occurrence and distribution of the various metallic ores belongs to the science of *geology;* the study of the modes of procuring the ores is the province of the *miner* and *engineer;* whilst the processes by means of which the metal itself is obtained from the ore, although mainly dependent upon chemical principles, are generally classed as belonging to the branch science of *metallurgy.*

Classification of the Metals.

The metals can be conveniently grouped into classes, in which the several members possess certain properties and general characters in common.

Class I. Potassium Group.—This group contains the metals of the alkalis. 1, Potassium. 2, Sodium. 3, Cæsium. 4, Rubidium. 5, Lithium. (6, Ammonium.)—The metals of this class are monovalent; they are soft, easily fusible, volatile at higher temperatures; they combine with great force with oxygen, decompose water at all temperatures and form basic oxides, which are very soluble in water, yielding powerfully caustic and alkaline bodies, hydroxides, from which water cannot be expelled by heat. Their carbonates are soluble in water, and each metal forms only one chloride. Ammonium, NH_4, is added to the list of alkali-metals proper, from the general similarity of the ammoniacal salts to those of potash and soda.

These metals and their compounds are closely analogous in their properties, and they exhibit a remarkable relation as regards their atomic weights: thus sodium, which stands between potassium and lithium in properties, has a combining weight which is the arithmetic mean of the other two, $\frac{39{\cdot}04 + 7{\cdot}01}{2} = 23{\cdot}02$; so, too, rubidium, standing half way between cæsium and potassium, has a mean atomic weight, $\frac{133 + 39{\cdot}04}{2} = 86{\cdot}02$. (For further information see p. 264.)

Class II. Calcium Group.—This group contains the metals of the alkaline earths.—1, Calcium. 2, Strontium. 3, Barium. —The metals of this class are divalent; they cannot be reduced by hydrogen or carbon alone; they decompose water at all temperatures, producing oxides, which combine with water to form hydroxides, from some of which the water can be driven off by heat. Their carbonates are insoluble in water, but soluble in water containing carbonic acid in solution.

Class III. Zinc Group.—1, Beryllium (or Glucinum). 2, Magnesium. 3, Zinc. 4, Cadmium.—These metals are divalent; they are all volatile at high temperatures, and burn when heated in the air: they decompose water at a high temperature, or in presence of an acid, and form only one oxide and one chloride.

Class IV. Lead Group.—1, Lead. 2, Thallium.—Heavy metals allied in their general properties to the first two classes. Lead is divalent, but thallium is monovalent.

Class V. Copper Group.—1, Copper. 2, Mercury. 3, Silver.—These dyad metals do not decompose water under any circumstances; they are oxidized by nitric and strong sulphuric acids; each of these metals forms two basic oxides which, except in the case of copper, are decomposed by heat alone.

Class VI. Cerium Group.—1, Scandium. 2, Yttrium. 3, Cerium. 4, Lanthanum. 5, Didymium. 6, Erbium. 7, Ytterbium. 8, Samarium.—This group contains a number of rare metals which at a high temperature decompose water and form basic sesquioxides insoluble in water.

Class VII. Aluminium Group.—1, Aluminium. 2, Gallium. 3, Indium.—These metals decompose water at a high temperature and form basic sesquioxides insoluble in water.

The metals of this group are distinguished from those of the preceding group by the power their sulphates possess of forming a peculiar class of double salts, termed alums, with the sulphates of the alkalis. The last two are rare metals.

Class VIII. Iron Group.—1, Manganese. 2, Iron. 3, Cobalt. 4, Nickel.—These are not volatile at the temperature of our furnaces; they decompose water at a high temperature, like the preceding class, and they form several oxides, chlorides, and sulphides.

Class IX. Chromium Group.—1, Chromium. 2, Molybdenum. 3, Tungsten. 4, Uranium.—These metals decompose water at a high temperature, and form trioxides which act as acid-forming oxides giving rise to a well-marked class of salts; they also yield volatile hexachlorides.

Class X. Tin Group.—1, Tin. 2, Titanium. 3, Zirconium. 4, Thorium. 5, Germanium.—Tin is the only one of this class employed in the arts. These metals decompose water at high temperatures and in presence of alkalis: they form dioxides and volatile tetrachlorides, and are tetravalent and closely connected with silicon.

Class XI. Antimony Group.—1, Antimony. 2, Bismuth, 3, Vanadium. 4, Niobium. 5, Tantalum.—The metals of this class are trivalent; they form the junction between the metals and metalloids, and they closely resemble arsenic, phosphorus, and nitrogen in their properties, and like these they yield pentoxides which are acid-forming bodies.

Class XII. Gold and Platinum Group.—1, Gold. 2, Platinum. 3, Palladium. 4, Rhodium. 5, Ruthenium. 6, Iridium. 7, Osmium.—Gold and platinum are not acted upon by nitric acid, but only by chlorine or aqua regia, and the oxides are reduced by heat alone; and they with silver and mercury constitute the noble metals. Gold is trivalent, and platinum is tetravalent. The remaining members of this group always occur together with platinum, and are therefore termed the *platinum metals.*

Physical Properties of the Metals.

Specific Gravity.—The following table, giving the specific gravities of the most important metals (water at 0° C = 1·00), shows the great variation which they exhibit in this respect:—

Table of Specific Gravities.

Osmium	22·5	Iron	7·8
Iridium	22·4	Tin	7·3
Platinum	21·5	Zinc	6·9
Gold	19·3	Antimony	6·7
Mercury	13·596	Arsenic	5·9
Thallium	11·8	Chromium	7·3
Palladium	11·4	Aluminium	2·67
Lead	11·4	Strontium	2·54
Silver	10·5	Magnesium	1·74
Bismuth	9·8	Calcium	1·58
Copper	8·9	Rubidium	1·52
Nickel	8·8	Sodium	0·974
Cadmium	8·6	Potassium	0·865
Cobalt	8·5	Lithium	0·594
Manganese	8·0		

Fusibility.—The melting-points of the metals differ even more widely than their densities; mercury fusing at 40° below zero, and the metal gallium at +30°, whilst platinum does not melt until the highest temperature of the oxyhydrogen blowpipe has been reached.

List of Melting-points.

Mercury	−40°	Antimony	425°
Gallium	+30°	Zinc	433°
Potassium	62°·5	Silver	1,000°
Sodium	95°·6	Copper	1,090°
Tin	235°	White Cast Iron	1,050°
Bismuth	270°	Grey ditto	1,200°
Cadmium	315°	Steel	1,300° to 1,400°
Lead	334°	Wrought Iron	1,500° to 1,600°

Other Physical Properties.—Some of the metals can be easily converted into vapour, or volatilized: thus mercury boils at 350°, and zinc at 940°, arsenic passes into vapour even before it assumes the liquid form, whilst potassium, sodium, magnesium, zinc, and cadmium can be distilled at a red-heat. Even the more infusible of the metals, such as copper and gold, are not absolutely fixed, but give off small quantities of vapour when strongly heated in a furnace.

The colour of most of the metals is nearly uniform, varying from the bright white of silver to the bluish-grey of lead; copper is the only red-coloured metal known, whilst gold, strontium, and calcium are yellow. In ductility, or the power of being drawn out into wire, and malleability, or the power of being hammered out into thin sheets, the metals differ considerably. Gold is the most malleable of all the metals, and is capable of being beaten out to the thickness of $\frac{1}{200000}$th part of an inch : it is, likewise, the most ductile metal. Other metals possess this property in lesser degree, whilst some, such as antimony and bismuth, are brittle, and may easily be powdered. Hardness, brittleness, and tenacity are physical properties of great importance, in which the metals differ widely.

Chemical Properties of the Metals.

The metals combine (1) with each other to form alloys; (2) with the non-metals to form oxides, sulphides, chlorides, &c. In the alloys the metallic appearance and properties are preserved, whereas in the compounds with the metalloids the physical properties of the metals as a rule disappear.

Alloys.

The compounds formed by the metals amongst themselves are not so definite as those which are formed by union with a non-metal ; nevertheless the alloys are largely used in the arts, as they possess many valuable properties not exhibited by the metals separately. Thus gold and silver are too soft to be used alone as a medium of currency, but the addition of 7·5 per cent. of copper gives an alloy of the requisite hardness. Then copper is too soft and tough to be wrought in the lathe, but when alloyed with half its weight of zinc it forms a hard and most useful substance known as brass. Gun-metal, or bronze, is a hard and tenacious alloy of 90 parts of copper and 10 of tin. Bell-metal, a still harder alloy, contains the same metals in the proportion of 80 of the former to 20 of the latter; whilst an alloy of 33 parts of tin to 67 of copper possesses a white colour, takes a high polish, and is known as speculum-metal, and employed for the reflectors of telescopes. For making printing type a peculiar alloy is employed, containing 80 parts of lead to 20 of antimony: this possesses many properties, necessary for type metal, which are found to belong to no single metal or other alloy.

The chemical composition of the alloys is not so definite or so well marked as that of the other metallic compounds, but they may frequently be obtained in crystals, in which the constituents are contained in atomic proportions. The melting point of an alloy is often much lower than the melting points of its constituent metals. Thus lead melts at 334°, bismuth at 270°, tin at 235°, and cadmium at 315°; whereas an alloy of two parts bismuth, 1 of tin and 1 of lead, melts at 95° to 98°, and one containing 8 of lead, 15 of bismuth, 4 of tin, and 3 of cadmium softens at as low a temperature as 60°, and is perfectly fluid at 65°. Potassium and sodium also unite together forming an alloy which is liquid at the ordinary temperature. The alloys of metals with mercury are termed *Amalgams*.

Absorption of Hydrogen by certain Metals.

Hydrogenium.—There are many chemical reasons for supposing that hydrogen is the vapour of a highly volatile metal, and not only is liquid hydrogen said to possess a steel-blue colour, but it has also been found possible to absorb hydrogen by certain metals. Thus, for instance, metallic palladium takes up no less than 982 volumes of hydrogen gas, forming a veritable alloy of the metal with *hydrogenium*, or hydrogen in its solid form. From the increase in bulk (owing to absorption of hydrogen) which the palladium undergoes when placed as the negative electrode in acidulated water, the density of hydrogenium has been found to be 0·733; it has also been shown to conduct heat and electricity, and to be magnetic, in these respects acting like a metal. Other metals than palladium, such as platinum and iron, possess this same power of condensing hydrogen, but to a less extent. The fact that red-hot platinum and iron are porous for hydrogen may be explained by the absorption (or *occlusion*) of this gas on the one side of the metallic tube or plate and its evaporation at the other side. A metallic meteorite (Lenarto) has been found to contain about twice its volume of absorbed hydrogen, whilst in terrestrial iron carbonic oxide gas is chiefly found to be absorbed. Hence we may conclude that the Lenarto meteorite had its origin in an atmosphere in which hydrogen gas predominates. (See Spectrum Analysis.)

Compounds of the Metals with Non-metals.

Metallic Oxides.—Oxygen acts very differently on the different metals. Some metals, such as zinc, magnesium, and calcium, take fire when heated, and burn with the evolution of intense light; whilst others, such as gold and silver, do not combine directly with oxygen, and are only obtained in combination with it by indirect means and with difficulty.

The oxides differ widely in properties and composition: they may, however, all be represented as water in which the hydrogen has been replaced by metal. Thus the monoxides may be considered to be water in which either each atom of hydrogen is replaced by a monad, as K_2O, Ag_2O, or the two atoms of hydrogen may be replaced by a dyad, as BaO, ZnO; whilst the higher oxides are regarded as two or more molecules of water, in which the hydrogen is in like manner replaced by its equivalent of metal. The most important of these higher oxides are the sesquioxides, such as alumina, Al_2O_3, and ferric oxide, Fe_2O_3; the dioxides, such as black oxide of manganese, MnO_2; the trioxides, as chromium trioxide, CrO_3.

The oxides may be divided into (1) *Basic oxides*; (2) *Peroxides*; (3) *Acid-forming oxides.*

Basic Oxides.— If only a portion of the hydrogen in water be replaced by metal, the resulting compound is termed a *Hydroxide:* thus by the action of potassium on water, hydrogen is liberated and caustic potash, KOH, potassium hydroxide, is formed. The hydroxides of the dyad metals may be considered as two molecules of water in which one atom of metal replaces two atoms of hydrogen; thus calcium hydroxide is $Ca(OH)_2$. The hydroxides corresponding to

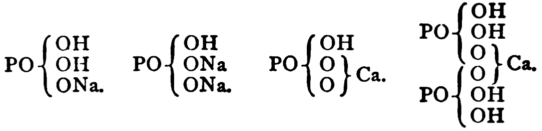
Normal and Acid Salts.—If all the replaceable hydrogen in an acid be exchanged for metal, a ***normal salt*** is said to be formed; if only a portion of the hydrogen be replaced, the resulting compound is termed an ***acid salt***: thus

$$KCl, \quad KNO_3, \quad K_2SO_4, \quad CaSO_4, \quad Na_3PO_4,$$

are all normal salts; $KHSO_4$ is an acid salt. Dibasic acids form both a normal and an acid salt with monad metals, but only a normal salt with dyad metals, thus:

$$SO_2OH.OK. \quad SO_2(OK)_2. \quad SO_2O_2Ca.$$

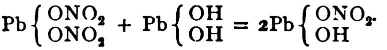
Polybasic acids yield several acid salts: thus



$$PO\left\{\begin{matrix}OH\\OH\\ONa.\end{matrix}\right. \quad PO\left\{\begin{matrix}OH\\ONa\\ONa.\end{matrix}\right. \quad PO\left\{\begin{matrix}OH\\O\\O\end{matrix}\right.\left.\begin{matrix}\\ \\ \end{matrix}\right\}Ca. \quad \begin{matrix}PO\left\{\begin{matrix}OH\\OH\\O\end{matrix}\right.\\PO\left\{\begin{matrix}O\\OH\\OH\end{matrix}\right.\end{matrix}\left.\begin{matrix}\\ \\ \end{matrix}\right\}Ca.$$

The greater the number of atoms of replaceable hydrogen contained in any acid, the greater will of course be the number of acid salts which this acid is capable of forming: thus we have Na_3PO_4; Na_2HPO_4; NaH_2PO_4; H_3PO_4.

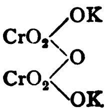
Basic salts are those formed by the combination of a normal salt with a basic oxide or hydroxide, thus:



$$Pb\left\{\begin{matrix}ONO_2\\ONO_2\end{matrix}\right. + Pb\left\{\begin{matrix}OH\\OH\end{matrix}\right. = 2Pb\left\{\begin{matrix}ONO_2.\\OH\end{matrix}\right.$$

This basic lead nitrate is obtained by boiling a solution of lead nitrate with lead hydroxide.

Anhydro-Salts.—A fourth class of salts is formed by the combination of a normal salt with an anhydride or acid-forming oxide. These salts were formerly also called acid salts; they are now generally termed anhydro-salts. One of the most common is potassium anhydro-chromate or bichromate of potash, $K_2Cr_2O_7$; this is a compound of the normal salt K_2CrO_4, with chromic anhydride or chromium trioxide, CrO_3.



The constitution of the other classes of salts will be best understood from the special descriptions.

Many of the metallic salts when crystallized contain a definite number of molecules of water; and this is termed *water of crystallization.*

Metals also unite with nitrogen, phosphorus, boron, silicon, carbon, and hydrogen; such of these compounds as deserve mention in these Lessons will be found described under the special heads.

LESSON XIX

CRYSTALLOGRAPHY

Most chemical substances, when they pass from the liquid or gaseous into the solid state, assume some definite geometric form, or are said to *crystallise.* Crystals are produced when a substance, such as nitre, is dissolved in water and the solution allowed gradually to evaporate; or when a body, such as sulphur, is melted and allowed to solidify by cooling; or when a volatile substance, such as iodine or arsenic trioxide, is vaporised, and the vapour condensed on a cool surface. Many naturally occurring minerals exhibit very perfect crystalline forms. We are ignorant of the mode in which such crystals are in most cases produced, but we know that the process of their formation has been a very slow one; and we find that, in general, a crystal is larger and more perfect the more gradually it has been formed. Crystalline bodies exhibit, in addition to their regular form, a peculiar power of splitting in certain directions more readily than in others, called *cleavage;* and also in many cases the property of allowing the rays of light and heat to pass more readily in one direction than another, giving rise to the well-known phenomena of double refraction.

Inorganic bodies which do not exhibit these peculiarities, or assume crystalline structure, such as glass and glue, are said to be *amorphous.* But certain highly complicated structures found in the vegetable and animal world exhibit a structure which, although it is non-crystalline, is not devoid of arrangement, and to which the name *organised* or *cellular structure* has been given.

As a rule, every particular substance possesses a definite form in which it always crystallises, and by which it can be distinguished. When a crystal is formed, from aqueous solution, for example, the smallest visible particle possesses the complete form of the largest crystal, and simply increases in size without undergoing any change of form.

Systems of Crystallography.—It has been found possible to arrange the many thousand different known crystals in *six systems*, to each of which belongs a number of forms having some property in common. In order to classify these different crystals, the existence of certain lines within the crystal called *axes* is supposed, round which the form can be symmetrically built up. These axes are assumed to intersect in the centre of the crystal, and pass through from one side to the other.

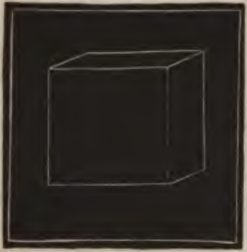


FIG. 44.

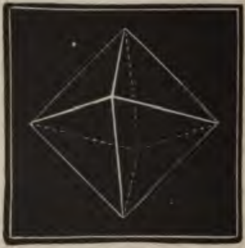


FIG. 45.

1*st*, or *Regular System.*—Three axes, all equal and at right angles.—The simplest forms of this system are (1) the cube (Fig. 44); (2) the regular octohedron (Fig. 45); (3) the rhombic dodecahedron (Fig. 46); and (4) the regular tetrahedron (Fig. 47). The following are a few of the substances crystallizing in this system—diamond, alum, common salt, fluor-spar, iron pyrites, and garnet.

2*nd*, or *Hexagonal System.*—Four axes, three equal and in one plane, making angles of 60°, and one longer or shorter, at right angles to the plane of the other three.—The regular six-sided prism (Fig. 48), the same with the addition of the regular six-sided pyramid (Fig. 49), and the rhombohedron (Fig. 50), are the common forms of this system. Quartz, calc-spar, beryl, corundum, graphite, ice (whose hexagonal form is seen in snow crystals), &c., crystallize in the hexagonal system.

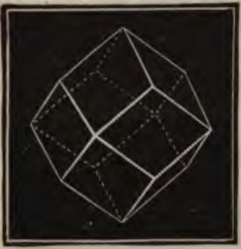


FIG. 46.

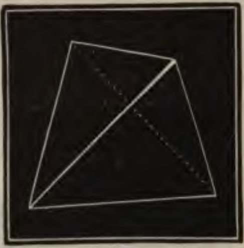


FIG. 47.

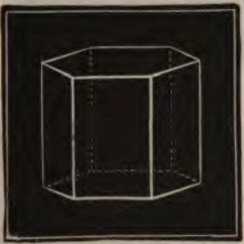


FIG. 48.

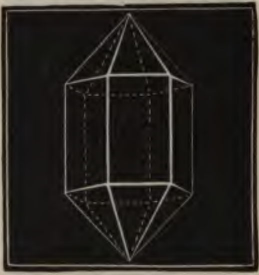


FIG. 49.

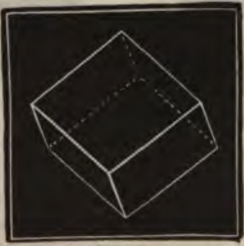


FIG. 50.

3rd, or *Quadratic System.*—Three axes, all at right angles, one shorter or longer than the other two.—The simple forms of this system are the first and second right square prisms (Figs. 51 and 52), and the first and second right square octohedra (Figs. 53 and 54). In the first square prism the axes terminate in the centre of each of the sides, and in the second the axes terminate at the intersection of the sides; and this is reversed with regard to the octohedra. Some of the common substances which crystallize in this system are—yellow prussiate of potash, zircon, and tin dioxide.

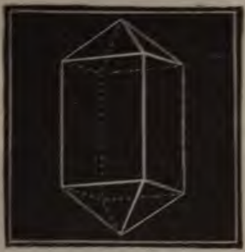


FIG. 51.

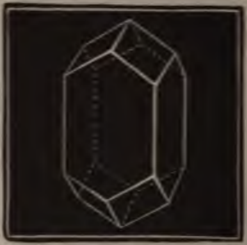


FIG. 52.

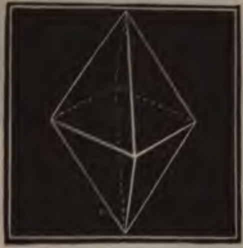


FIG. 53.

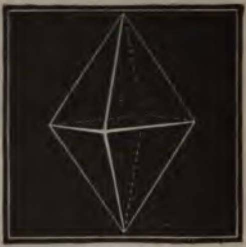


FIG. 54.

4th, or *Rhombic System.*—Three axes, all unequal, and all at right angles.—The chief forms of the crystals in this system are the right octohedron with rhombic base (Figs. 55 and 56), and the right rhombic prism (Fig. 57). In this system the following substances are found—nitre, barium sulphate, arragonite, topaz, and native sulphur.

5th Monoclinic or *Monosymmetric System.*—Three axes, all unequal: two cut one another obliquely, and one is at right angles to the plane of the other two.—The oblique rhombic octohedron (Fig. 58) belongs to this system. Many substances crystallize in this system; amongst the most common are—sulphur deposited from fusion, sodium carbonate and phosphate, ferrous sulphate, borax, and cane sugar.

6*th*, *Triclinic* or *Asymmetric System*.—Three axes, all unequal, and all oblique.—The doubly-oblique octohedron and the doubly-oblique prism (Fig. 59) are the leading forms in this system. Copper sulphate, boric acid, the mineral albite, potassium bichromate, and a few other substances are to be found to crystallize in this system, the forms of which are in general very complicated. The crystalline form of copper sulphate is shown in Fig. 60.

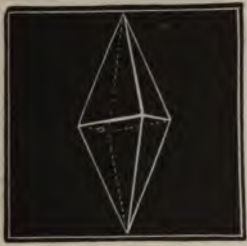


FIG. 55.

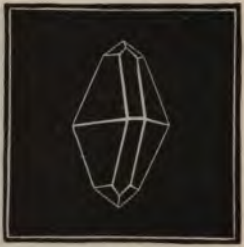


FIG. 56.

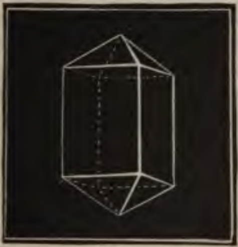


FIG. 57.

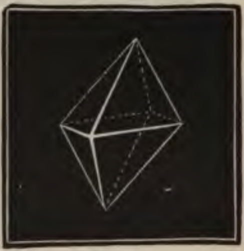


FIG. 58.

Under one or other of these six divisions all the known forms of crystals can be classed. In every distinct crystal belonging to any one of these systems, in which the axes are not all equal, or all at right angles, certain relations exist between the lengths of the axes, and these have certain mutual inclinations to one another. These relations and inclinations vary with different substances, but are constant for the same; so that different bodies, all crystallizing in the same system, as a rule, have different relations between the lengths of the axes, and these generally have different inclinations to one another.

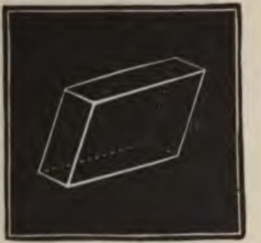


FIG. 59.

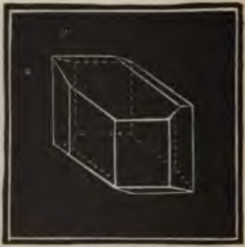


FIG. 60.

Isomorphism and Dimorphism.—Certain substances exhibiting a similarity in their chemical constitution are found to crystallize in the same forms; these are said to be *isomorphous;* whilst, when the same body occurs crystallized in two different systems, it is said to be *dimorphous*. Examples of these peculiar relations between chemical composition and crystalline form will be given later on.

LESSON XX

CLASS I.—THE POTASSIUM GROUP

Potassium, Sodium, Cæsium, Rubidium, Lithium, Ammonium

POTASSIUM

Symbol K (*kalium*), *Atomic Weight* 39·04, *Specific Gravity* 0·865.—The metal potassium was discovered in the year 1807, by Sir Humphry Davy, who decomposed the alkali potash into the metal, hydrogen, and oxygen, by means of a powerful galvanic current. Before this time the alkalis and alkaline earths were supposed to be elementary bodies. The metal is now prepared by heating together potash and carbon to a high temperature in an iron retort. The carbon at the high temperature is able to take the oxygen from the potash, forming carbon monoxide, which escapes as a gas, whilst the metal potassium, which is volatile at a red heat, distils over. The preparation of this metal is attended with many difficulties, and requires special precautions, as the vapour of potassium not only takes fire when brought in contact with the air, but decomposes water, combining with the oxygen and liberating hydrogen. Hence the metal was formerly condensed in a receiver filled with rock-oil; a black explosive compound of the metal with carbon monoxide was thus frequently formed, and caused several fatal accidents. The vapour of the metal is now condensed as it comes out of the retort, in a hollow cast-iron box, from which the liquid metal drops into a vessel placed below containing petroleum. The arrangement of furnace, retort, and condenser is seen in Fig. 61.

Potassium, thus prepared, is a bright, silver-white metal, which can be easily cut with a knife at the ordinary atmospheric temperature; it is brittle at 0°, melts at 62°·5, and does not become pasty before melting; when heated to a temperature below red heat, potassium sublimes, yielding a fine, green-coloured vapour. This metal rapidly absorbs oxygen when exposed to the air, and gradually becomes converted into a white oxide. Thrown into water, one atom of potassium displaces one of hydrogen from the water, forming potassium hydroxide, or caustic potash, KOH. This takes place with such force that the heat developed is sufficient to ignite the hydrogen thus set free, and the flame becomes tinged with the peculiar purple tint characteristic of the potassium compounds, whilst the water attains an alkaline reaction from the potash which is formed. Potassium also combines directly with chlorine and sulphur, and many other non-metals, evolving heat and light.

Sources of the Potassium Compounds.—The original source of potassium compounds is the felspar of the granitic rocks of which the earth is composed, as these contain from two to three per cent. of this metal. Up to the present time, this source has not been used for the manufacture of the potassium salts, as no cheap and easy mode has yet been made available for separating the potash from the silicic acid, with which it is combined in felspar. Plants, however, are able slowly to separate out and assimilate the potash from these rocks and soils : so that by burning the plant and extracting the ashes with water, a soluble potassium salt is obtained. This is the crude potassium carbonate, called, when purified by re-crystallization, *pearl-ash* ; and it is from this substance that a large number of the potassium compounds are ob-

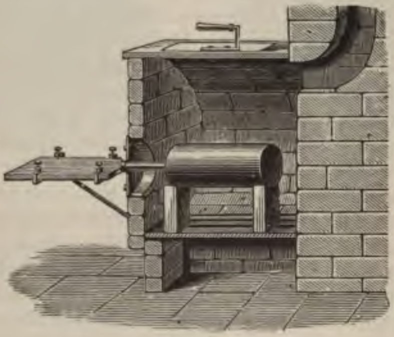


FIG. 61.

tained. Some of the other potassium salts, such as the nitrate and chloride are found in large quantities in various localities as deposits on the surface, or in the interior, of the earth. The chief source of potassium compounds at the present time is the large deposit of salts at Stassfurt in Germany, where potassium chloride occurs in beds together with rock salt. These beds also form the most important source of bromine (p. 110). Another inexhaustible source of potassium compounds is sea-water: a plan has been proposed by which those compounds can be obtained from the sea.

Potassium Oxides.—Potassium combines with oxygen in two proportions, viz. :—

(1) Potassium monoxide . . . . K_2O;
(2) Potassium peroxide . . . . K_2O_4.

Potassium Monoxide, K_2O, is obtained by allowing thin pieces of the metal to oxidize in dry air; it is a greyish-white, brittle substance, which melts a little above red-heat, and volatilizes only at a very high temperature. This oxide combines with water with evolution of great heat, producing potassium hydroxide, or caustic potash, from which water cannot again be separated by heat. The reaction may be represented as an exchange of hydrogen for potassium:

$$K_2O + H_2O = 2KOH.$$

The *Peroxide* is produced when potassium is oxidized at high temperatures.

Potassium Hydroxide, or *Caustic Potash*, KOH, is prepared by boiling one part of potassium carbonate with twelve parts of water, and adding slaked lime prepared from two-thirds part of quicklime. In this reaction calcium carbonate (chalk) is formed, which falls to the bottom as a heavy powder, caustic potash remaining in solution. The clear liquid, which should not effervesce on addition of an acid, is evaporated in a silver basin to dryness, fused by exposure to a stronger heat and cast into sticks in a metallic mould. Thus prepared caustic potash is a white substance, soluble in half its weight of water, and acts as a powerful cautery, destroying the skin. It is largely used in the arts and manufactures for soap-making, and is employed in the laboratory for various purposes.

Salts of Potassium.

Potassium Carbonate, K_2CO_3.—This salt receives the commercial name of potashes, or pearl-ashes, and is imported in large quantities from Russia and America. The crude substance is prepared by boiling out the ashes of plants with water, and evaporating the solution to dryness: a pure salt may be afterwards obtained by crystallization. The leaves and small twigs of plants contain more potash than the stems and large branches. Potassium carbonate can be obtained perfectly pure by heating pure potassium tartrate to redness, and separating the carbonate formed by dissolving in water. This salt absorbs water from the air, or is *deliquescent*, and is, therefore, very soluble in water; it also turns red litmus blue, possessing a strongly alkaline reaction.

Hydrogen Potassium Carbonate (*Bicarbonate of Potash*), $HKCO_3$.—This substance is formed when a current of carbonic acid gas, CO_2, is passed through a strong solution of the preceding salt. It may be considered as dibasic carbonic acid, H_2CO_3, in which one atom of hydrogen is replaced by one of potassium. It is a white salt, not so soluble as potassium carbonate; its solution is nearly neutral to test paper.

Potassium Nitrate (*Nitre or Saltpetre*), KNO_3.—This important salt occurs as an efflorescence on the soil of several dry tropical countries, especially that of India. It may be artificially prepared by the process of "nitrification," in which animal matter (containing nitrogen) mixed with wood-ashes and lime is exposed in heaps to the action of the air; the organic matter gradually undergoes oxidation, nitric acid being formed; and this unites with the lime and the potash to form nitrates. The salt is obtained from both of these sources by boiling out the soil or deposit with water, adding potassium carbonate to decompose the nitrate of calcium, and allowing the nitre to crystallize out. Nitre crystallizes in rhombic prisms, dissolves in seven parts of water at 15°, and in its own weight of hot water. It contains nearly half its weight of oxygen, with which it parts on heating with carbon or other combustible matter; for this reason, nitre is largely used in the manufacture of gunpowder and fireworks.

Gunpowder consists of an intimate mixture of nitre, charcoal, and sulphur. The decomposition which occurs when gunpowder is fired may be generally expressed by saying that the oxygen of the nitre combines with the charcoal, forming carbonic acid and carbonic oxide, whilst the nitrogen is liberated, and the sulphur combines with the potassium. Hence gunpowder can burn under water or in a closed space, as it contains the oxygen needed for the combustion in itself; and the great explosive power of the substance is due to the violent evolution of large quantities of gas, and a rapid rise of temperature, causing an increase of bulk sudden and great enough to produce what is termed an explosion. It has been found by practice that the best gunpowder is that which contains nearly two molecules of nitre to one atom of sulphur and three of carbon; but the decomposition which actually occurs in the explosion is a more complicated one than has been expressed above, and cannot be represented in an equation. The following table gives the composition of musketry powder, as manufactured by different nations:

	English and Austrian.	Prussian.	Chinese.	French.
Nitre	75	75	75·7	75·0
Charcoal	15	13·5	14·4	12·5
Sulphur	10	11·5	9·9	12·5
	100	100·0	100·0	100·0

Potassium Chloride, KCl.—This salt occurs in certain saline deposits, as at Stassfurt, and also exists in large quantities in sea-water: it crystallizes in cubes like sodium chloride, and is now much employed for the preparation of other potassium salts.

Potassium Chlorate, $KClO_3$.—The action of chlorine on potash and the production of this salt have been already explained (see page 107). It is manufactured on the large scale by decomposing calcium chlorate, made by saturating hot milk of lime with excess of chlorine, by means of potassium chloride, thus:

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

Potassium chlorate being but slightly soluble in cold water separates out in large tabular crystals, whilst the soluble calcium chloride remains dissolved. It is used for the preparation of oxygen gas, for pyrotechnic purposes, in the manufacture of lucifer matches, and in calico-printing as an oxidising agent.

Potassium Iodide, KI.—A very soluble salt, crystallizing in cubes, obtained by dissolving iodine in solution of caustic potash, evaporating, and igniting the solid mass. Iodide of potassium is used in photography, and acts as a valuable medicine.

Potassium Sulphate, K_2SO_4, is contained in the ashes of both sea- and land-plants, and is only slightly soluble in water. A second sulphate, termed hydrogen potassium sulphate, $HKSO_4$ (or bisulphate of potash) is a soluble salt obtained in the process of the manufacture of nitric acid.

Potassium Sulphides.—Potassium combines with sulphur to form several compounds of which the best known are K_2S, K_2S_2, K_2S_3, and K_2S_5. They are soluble substances, which evolve sulphuretted hydrogen when heated with an acid, and are not used in the arts.

By passing sulphuretted hydrogen gas into a solution of caustic potash until it is saturated, a compound termed *hydrogen potassium sulphide*, HKS, is formed.

General Characteristics of the Potassium Compounds.

All the potassium compounds impart a violet colour to the flame, and the spectrum of this flame (see Frontispiece, Spectrum No. 2; also p. 266, Spectrum Analysis) is distinguished by the presence of two bright lines; one in the red, and another in the violet. Almost all the potassium salts are soluble in water: the three which are least soluble are—(1) potassium perchlorate; (2) hydrogen-potassium tartrate (cream of tartar), which is precipitated in the form of a white crystalline powder, when a solution of a potassium salt is mixed with an excess of tartaric acid: and (3) potassium platinichloride, $2(KCl)+PtCl_4$, which separates in small yellow cubical crystals, when platinic chloride solution is added to a soluble potassium salt. These reactions serve to distinguish the potassium salts.

SODIUM.

Symbol Na (*natrium*), *Atomic Weight* 22·99, *Specific Gravity* 0·97.—This metal was discovered by Davy immediately after the isolation of potassium, by the decomposition of soda with the galvanic current, and it is now manufactured in large quantities for the preparation of other metals, especially magnesium and aluminium. The method of manufacture adopted until recently was similar to that described for potassium, viz. heating carbon and sodium carbonate. An improvement was then made in the process by heating caustic soda with a compound of iron and carbon, the sodium distilling over. In place of these methods of distillation sodium is now largely manufactured by the electrolysis of caustic soda, the metal being thus obtained directly in the liquid condition: it is now sold at 4*s*. per lb. Sodium is a silver-white metal, soft at ordinary temperatures, and melting at 95°·6; it volatilizes below a red-heat, yielding a colourless vapour. When thrown upon water it floats, and rapidly decomposes the water with disengagement of hydrogen, soda being formed. If the water be hot or be thickened with starch, the globule of metal becomes so much heated as to enable the hydrogen to take fire. The compounds of sodium are very widely diffused, being contained in every speck of dust (see Spectrum Analysis, p. 266); they exist in enormous quantities in the primitive granitic rocks (see p. 8), but they are most readily obtained from sea-water, which contains nearly three per cent. of sodium chloride (common or sea-salt), or from the large deposits of this substance which occur in Cheshire, Galicia, &c. Sodium carbonate was formerly obtained from the ashes of sea-plants or kelp, as potassium carbonate is still prepared from the ashes of land plants; but at present the sodium carbonate is altogether manufactured, on an enormously large scale, from common salt.

Sodium Oxides.—There are two compounds of sodium and oxygen known—Sodium Oxide, Na_2O; and Sodium Dioxide, Na_2O_2.

Sodium Oxide, Na_2O, is formed when sodium is oxidized in dry air or oxygen at a low temperature, a white powder being formed: this takes up moisture with great avidity, forming NaOH, *sodium hydroxide*, or *caustic soda*, from which water cannot again be separated by heat alone, but which can be converted into the oxide by heating with sodium; thus:

$$NaOH + Na = Na_2O + H.$$

Sodium Dioxide, Na_2O_2, is a yellowish-white powder, which is formed when sodium is heated in oxygen to 200°; it is soluble in water, but the solution readily decomposes, giving off oxygen and leaving sodium hydroxide.

Sodium Hydroxide, or Caustic Soda, NaOH, is a white solid substance, fusible below a red-heat, and less volatile than the corresponding potassium compound. It is very soluble in water, acts as a caustic, is powerfully alkaline, and is largely used in soap-making. The manufacture of solid caustic soda is now carried on on a large scale, by boiling lime and sodium carbonate together with water, and evaporating down the clear solution, when a white fibrous mass remains. It deliquesces in the air, and when moist absorbs carbon dioxide; it melts at about a red-heat:

$$Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2NaOH.$$

Salts of Sodium.

Sodium Chloride (*Common Salt*), NaCl.—It is from this salt that almost all the other sodium compounds are prepared. Sodium chloride occurs in thick beds in various parts of the world, especially in Cheshire, Galicia, Tyrol, Spain and Transylvania. It is likewise prepared from sea-water by evaporation or by freezing; and from certain brine springs by evaporation. When slowly deposited sodium chloride crystallizes in large regular cubes. It is soluble in about two and a half parts of water at 15°, and dissolves very little more in hot than in cold water.

Sodium Carbonate, Na_2CO_3.—This substance, known in commerce as ***soda-ash***, is manufactured in England on an enormous scale, and used for glass-making, soap-making, bleaching, and various other purposes in the arts. Formerly it was prepared from barilla or the ashes of sea-plants, but now it is wholly obtained from sea-salt by a series of chemical decompositions. The first and older mode of manufacture is termed, from its discoverer, the Leblanc process. The second and newer method is called the ammonia soda process.

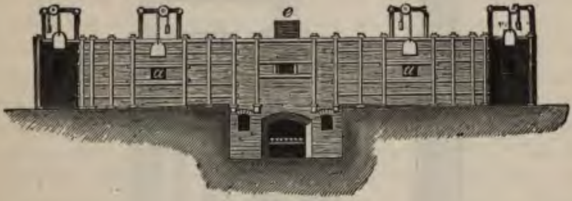


FIG. 62

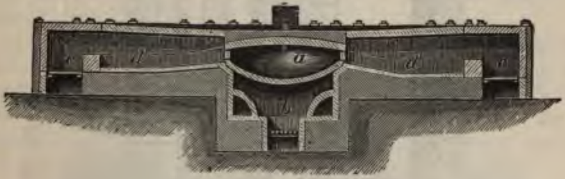


FIG. 63.

The Leblanc process may be divided into two stages. (1) Manufacture of sodium sulphate, or salt-cake, from sodium chloride (common salt); called salt-cake process. (2) Manufacture of sodium carbonate, or soda-ash, from salt-cake; called black-ash process.

(1) *Salt-cake Process.*—This process consists in the decomposition of salt by means of sulphuric acid, and is effected in a furnace called the *Salt-cake Furnace*; Fig. 62 shows the elevation, and Fig. 63 the section, of such a furnace. It consists of (1) a large covered iron pan (*a*) placed in the centre of

the furnace, and heated by a fire placed underneath ; and (2) two roasters or reverberatory furnaces (*dd*) placed one at each end, and on the hearths of which the salt is completely decomposed. The charge of half a ton of salt is first placed in the iron pan, and then the requisite quantity of sulphuric acid allowed to run in upon it. Hydrochloric acid gas is evolved, and escapes through a flue (*e*) with the products of combustion into towers, or scrubbers, filled with coke or bricks moistened with a stream of water ; the whole of the acid vapours are thus condensed, and the smoke and heated air pass up the chimney. A drawing of a good arrangement of the kind is given in Fig. 64. The acid fumes from the salt-cake furnace enter the tower B, which is sixty feet in height, by the flue A ; passing up this tower it meets with the descending current of water. The dilute acid thus formed

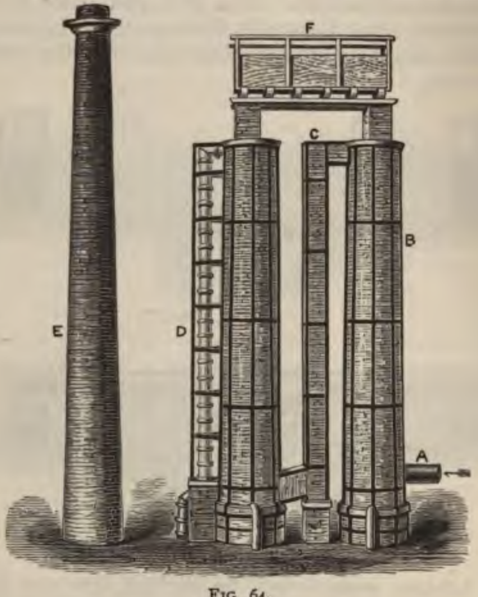


FIG. 64.

runs away by a pipe seen at the base of the tower, whilst the unabsorbed fumes and products of combustion pass down the brick tunnel C into the second tower, in which they ascend, and meet another current of falling water. When the vapours reach the top of this tower, they are perfectly free from hydrochloric acid gas, and are allowed to pass through the stoneware pipes D to the chimney E. By Act of Parliament the alkali-makers are compelled to condense at least 95 per cent. of the hydrochloric acid gas they produce, and no escape of more than 0·2 grain of hydrochloric acid per cubic foot of air is permitted from any chimney. So perfectly is this condensation as a rule carried out, that the escaping gases frequently do not cause a turbidity in a solution of silver nitrate, proving the absence of even a trace of the acid gas. After the mixture of salt and acid has been heated for some time in the iron pan, and has become solid, it is raked by means of the doors (*a a*) seen in Fig. 62, on to the hearths of the furnaces at each side of the decomposing pan, where the flame and heated air of the fire complete the decomposition into sodium sulphate and hydrochloric acid. The hydrochloric acid is a most valuable product, being used for the manufacture of bleaching powder (see p. 105).

(2) *Black-ash Process.*—This process consists (1) in the preparation of sodium carbonate, and (2) in the separation and purification of the same. The first chemical change which the salt-cake undergoes in its passage to soda-ash is its reduction to sulphide, by heating it with powdered coal or slack:

$$Na_2SO_4 + C_4 = Na_2S + 4CO.$$

The second decomposition is the conversion of the sodium sulphide into sodium carbonate, by heating it with chalk or limestone (calcium carbonate):

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

These two reactions are in practice carried on at once; a mixture of ten parts of salt-cake, ten parts of limestone, and seven and a half parts of coal being heated in a reverberatory furnace called the *Balling Furnace* (shown in section in Fig. 65, and in elevation in Fig. 66), until it fuses and the above decomposition is complete, when it is raked out into iron wheelbarrows to cool. This process is generally termed the *black-ash process*, from the colour of the fused mass.

The next operation consists in the separation of the sodium carbonate from the insoluble calcium sulphide and other impurities. This is easily accomplished by *lixiviation*, or dissolving the former salt out in water. To evaporate down the solution, the waste heat of the black-ash furnace is used, the heated air passes over an iron pan (see *b*, Fig. 65) containing the liquid. On calcining the residue, the soda-ash of commerce is obtained.

Ammonia-Soda Process.—During the last few years the Leblanc system of making alkali has to a considerable extent been superseded by a new and quite different process. This depends upon the fact that if a solution of chloride of sodium (brine) be saturated with ammonia gas, and carbon dioxide passed into the liquid under pressure, a precipitate of sodium bicarbonate is thrown down, whilst sal-ammoniac (ammonium chloride) remains in solution:

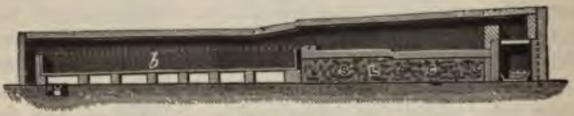


FIG. 65.

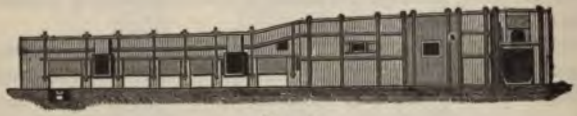


FIG. 66.

$$NH_3 + CO_2 + NaCl + H_2O = NaHCO_3 + NH_4Cl.$$

The bicarbonate of soda when dried and ignited, yields pure soda-ash. The sal-ammoniac is decomposed by caustic lime or magnesia and the ammonia thus liberated again used. In this process the whole of the chlorine of the common salt is now thrown away as the chloride of calcium or of magnesium. Hence by this plan bleaching powder cannot be prepared. If an economical plan for liberating the chlorine from either of the above-named salts be discovered, this process (termed the Solvay process from its discoverer) will in time altogether displace the older method of Leblanc.

No less than 700,000 tons of common salt are annually consumed in the alkali works of Great Britain, for the preparation of nearly the same weight of soda-ash, of which the value is about three millions sterling. The soda-ash of commerce contains from 48 to 56 per cent. of sodium monoxide, Na_2O, as carbonate and hydrate, the remainder being impurities, consisting generally of sulphate, sulphite, and chloride. If soda-ash be dissolved, and the saturated solution allowed to stand, large transparent crystals (monoclinic) of the hydrated carbonate, of the formula $Na_2CO_3 + 10H_2O$, separate out : this substance is commonly known as *soda-crystals*, and is much used for softening water for washing purposes. Sodium carbonate also occurs in small quantity in certain localities as an efflorescence on the soil, and in the beds of dried-up lakes.

Hydrogen Sodium Carbonate, or Bicarbonate of Soda, $NaHCO_3$, is obtained by exposing the crystallized carbonate to an atmosphere of carbonic acid gas. It is a white crystalline powder, which on heating is readily converted into sodium carbonate. The bicarbonate is chiefly used in medicine, and for the production of effervescing drinks.

Sodium Nitrate, $NaNO_3$, is found in large beds in Peru and Northern Chili, and termed soda- or Chili-saltpetre. It is imported in large quantities and used as a manure, and also in the preparation of nitric acid (being cheaper than nitre), and of nitre. For this latter purpose a hot concentrated solution of this salt is mixed with a hot saturated solution of potassium chloride : on cooling, sodium chloride separates out in crystals, and potassium nitrate remains in solution.

Sodium Sulphate, $Na_2SO_4 + 10H_2O$, is known in commerce as Glauber's salts, and in the anhydrous state as salt-cake. It occurs in the water of many mineral springs, and is used in medicine, whilst as salt-cake it is employed in large quantities in the glass manufacture.

Amongst the other more important salts of sodium are :

Sodium Thiosulphate, $Na_2S_2O_3 + 5H_2O$, commonly called hyposulphite of soda, already mentioned under the compounds of sulphur and oxygen, and largely used in photography (p. 129) ; the *Sodium phosphates*, mentioned under phosphorus (p. 148) ; *Borax*, $Na_2B_4O_7 + 10H_2O$ (see p. 142) ; *Sodium sulphide*, Na_2S, a soluble salt formed by reducing the sulphate with carbon ; *Sodium silicate*, or soluble glass (see p. 139).

General Characteristics of the Sodium Compounds.

All the sodium salts, with the single exception of the metantimoniate, are soluble in water. The presence of sodium compounds can be detected by the peculiar yellow tinge which they impart to the flame. The spectrum of sodium is distinguished by one fine bright double line, identical in position with the dark solar line called D (see Chromolith No. 7).

CÆSIUM AND RUBIDIUM.

Cs = 132·5. Rb = 85·2.

These two metals were discovered in 1860-61 by Bunsen and Kirchhoff, by means of spectrum analysis (see p. 268). They so closely resemble one another and potassium in their chemical properties, that they had previously been mistaken for the latter well-known metal. They are found widely distributed, although generally occurring in small quantities. They were originally discovered in the mineral water of Dürkheim ; but since that time they have been found in many other springs, in several kinds of mica and other old plutonic silicates, as well as in the ashes of several plants, viz., beet-root, tobacco, coffee, and grapes. These metals can be separated from potassium by the greater insolubility of the double chloride which they form with platinum ; if a mixture of potassium, cæsium, and rubidium salts be completely precipitated by platinic chloride, and the precipitate boiled out with water, the most insoluble residue will contain the new metals. Cæsium may be separated from rubidium by the greater solubility of the acid tartrate of the former metal. The salts of cæsium and rubidium are isomorphous with the corresponding potassium compounds. The fused chlorides of these metals are easily decomposed by the galvanic current, and the metallic element deposited. Rubidium (but not cæsium), can also be prepared by reduction with carbon, like potassium. It is a white metal which rapidly undergoes oxidation ; its specific gravity is 1·52 ; and it forms a greenish-blue vapour. The spectra of these metals are shown in Nos. 3 and 4 of the Chromolith.

LITHIUM.

Symbol Li, *Atomic Weight* 7·01, *Specific Gravity* 0·59. —This metal is prepared by decomposing the fused chloride by electricity : it is of a white colour, it fuses at 180°, and is the lightest metal known. The lithium salts were formerly supposed to be very rare, only being known to occur in three or four minerals, but spectrum analysis has shown that this is a widely-distributed substance : it occurs in small quantities in almost all waters, in milk, tobacco, and even in human blood. A spring in Cornwall contains large quantities of this metal in the form of chloride. Lithium in its chemical relations stands between the class of alkali- and alkaline-earth metals, the hydrate, carbonate, and phosphate being only sparingly soluble in water. All the volatile lithium compounds impart a magnificent crimson tinge to the flame, and the spectrum of this flame exhibits one bright and very characteristic red line, by means of which the presence of the minutest trace of this substance can be detected with certainty and ease. (See Chromolith No. 8.)

AMMONIUM AND THE SALTS OF AMMONIA.

The ammoniacal salts may conveniently be considered together with the class of alkali-metals, as in their chemical properties they present a remarkable analogy with the salts of the alkalis proper. In all these salts the existence of a quasi-metal called *Ammonium*, NH_4, is supposed : and if this substance be substituted for an atom of potassium or sodium in the alkali salts, a corresponding salt of ammonium is formed; thus:

Potassium Chloride, KCl.	Ammonium Chloride, NH_4Cl.
Potassium Sulphate, $\left.\begin{matrix}K\\K\end{matrix}\right\}SO_4$.	Ammonium Sulphate, $\left.\begin{matrix}NH_4\\NH_4\end{matrix}\right\}SO_4$.
Potassium Hydrosulphide $\left.\begin{matrix}K\\H\end{matrix}\right\}S$.	Ammonium Hydrosulphide $\left.\begin{matrix}NH_4\\H\end{matrix}\right\}S$.

The radical ammonium $\left.\begin{matrix}NH_4\\NH_4\end{matrix}\right\}$ has not obtained in the free state, but a singular compound, the so-called ammonium amalgam, can easily be prepared by placing sodium amalgam into a solution of ammonium chloride. Ammonium amalgam forms a singular light bulky metallic mass, which rises to the surface of the liquid, but soon decomposes into ammonia, hydrogen, and mercury.

Ammonium Chloride, NH_4Cl, or sal-ammoniac, is obtained by neutralizing the distilled ammoniacal liquor of the gas-works (see p. 91) with hydrochloric acid, and evaporating the liquor to dryness, or by subliming a mixture of the commercial sulphate of ammonium with common salt. The sublimed salt forms a tough fibrous mass; it is easily soluble in water, and crystallizes in arborescent forms composed of crystals belonging to the regular system. On heating, it volatilizes completely without melting.

Ammonium Carbonates.—The normal salt, $(NH_4)_2CO_3$, is a very unstable compound, which decomposes in contact with air, with evolution of ammonia, and is prepared by adding ammonia to one of the acid-salts. By heating a mixture of sal-ammoniac and chalk a white transparent salt sublimes, which is the carbonate of ammonia or *sal-volatile* of commerce. This is a mixture of the acid carbonate or the bicarbonate $H(NH_4)CO_3$, with carbamate, $NH_4CO_2NH_2$. It smells of ammonia, and absorbs water and carbonic acid gas from the air, passing into the bicarbonate. This latter salt is isomorphous with the corresponding potassium compound, and occurs frequently in guano.

Ammonium Nitrate, NH_4NO_3,—is obtained by neutralizing ammonia with nitric acid, and crystallizes in long transparent elastic needles. It is very soluble in water, and when heated above 230° decomposes into water and nitrous oxide gas (see p. 65).

Ammonium Phosphates.—The normal salt, $(NH_4)_3PO_4$, is formed when phosphoric acid and ammonia are mixed in concentrated solution, and on cooling, the salt separates out in crystals. On drying it loses ammonia, yielding the salt $(NH_4)_2HPO_4$, which crystallizes in the monoclinic system. On boiling the solution of the latter, the salt $NH_4H_2PO_4$, is formed, and may be crystallized in quadratic prisms. All these salts leave on ignition a residue of metaphosphoric acid. Ammonium sodium phosphate, $NH_4NaHPO_4+4H_2O$, or microcosmic salt, is a substance much used in blowpipe experiments.

Ammonium Sulphate, $(NH_4)_2SO_4$.—This salt is prepared on the large scale by adding sulphuric acid to gas-water; it also occurs native. The sulphate is largely employed for alum making, and especially as a manure.

Ammoniun Sulphide $(NH_4)_2S$.—If dry sulphuretted hydrogen and excess of dry ammonia gas be brought together at $-18°$ this compound separates out in colourless crystals. At the ordinary temperature the sulphide loses NH_3, and is converted into a crystalline mass of the *hydrosulphide* NH_4HS, a very volatile body, which decomposes above 50° into ammonia and sulphuretted hydrogen. An aqueous solution of this body is much used in the laboratory as a reagent; it is obtained by saturating aqueous ammonia with sulphuretted hydrogen gas; the colourless solution possesses a disagreeable smell, and soon becomes yellow from the formation of polysulphides of ammonium, and water.

General Characteristics of the Ammonium Compounds.

The salts of ammonia can easily be recognised by their giving off an alkaline gas possessing a pungent smell of ammonia when they are heated with caustic lime or a caustic alkali. The acid tartrate and the double platinic chloride are both insoluble, and resemble the corresponding potash compounds so closely that the two sets of salts cannot be distinguished by means of these tests. In order to test for potash in presence of ammoniacal salts, all the latter must first be driven off by heating. It is well to remember that ammonia, NH_3, is only the first term of a series of volatile bodies possessing closely similar properties and forming definite salts ; these compounds will be described in that part relating to organic chemistry.

HYDROXYLAMINE, NH_3O, or $N\begin{cases} OH \\ H \\ H. \end{cases}$

This substance, which may be regarded as a compound intermediate between ammonia and water, or as ammonia NH_3, in which one atom of hydrogen is replaced by hydroxyl (OH), is a base uniting with acids to form a well-defined series of salts. Hydroxylamine has not been isolated in the pure state, but its aqueous solution has been prepared, and forms a colourless, inodorous liquid, possessing a strong alkaline reaction. On distillation, a part of the base passes over unchanged, whilst the remainder undergoes decomposition with formation of ammonia. Hydroxylamine can be prepared synthetically by the direct union of nitric oxide and nascent hydrogen, thus : $NO + H_3 = NH_3O$; and also by the reduction of the nitrite and nitrate of ammonia. Hydroxylamine on treatment with nitrous acid yields nitrous oxide, just as ammonia yields nitrogen. It is a very important reagent, being largely employed in organic chemistry. The following are some of the best known salts of this base ; they correspond in constitution and in some of their properties to the salts of ammonia :—

Hydrochloride	of	Hydroxylamine	NH_3OHCl.
Sulphate	,,	,,	$(NH_3O)_2H_2SO_4$.
Nitrate	,,	,,	NH_3OHNO_3.
Phosphate	,,	,,	$(NH_3O)_3H_3PO_4$.

LESSON XXI

CLASS II.—THE CALCIUM GROUP

Calcium, Strontium, Barium

CALCIUM

Symbol Ca, *Atomic Weight* 39·9, *Specific Gravity* 1·58

Calcium forms a considerable portion (see p. 8) of the plutonic rocks of which the earth is composed, and occurs in very large quantities, forming whole mountain-chains of limestone, chalk, gypsum, and mountain limestone. The metal calcium is obtained by the decomposition of the chloride by the electric current, or by heating the iodide with sodium; it is a light yellow metal which easily oxidizes in the air, and when heated in air burns with a bright light, lime or calcium monoxide, CaO, being formed.

Calcium Monoxide, or *Lime*, CaO.—Pure lime is obtained by heating white or black marble to redness in a vessel exposed to the air. Lime is prepared on a large scale, for building and other purposes, by heating limestone (the carbonate) in kilns by means of coal mixed with the stone; the carbonic acid escapes, and *quick* or *caustic-lime* remains. Pure lime is a white, infusible substance, which combines with water very readily, giving off great heat, and falling to a white powder called calcium hydroxide, or *slaked lime*, $CaOH_2O$, or $Ca(OH)_2$. The hydrate is slightly soluble in water, 1 part of it dissolving in 730 parts of cold, but only in 1300 parts of boiling water, forming *lime-water*, which, like the hydrate, has a great power of absorbing carbonic acid from the air. It is indeed partly owing to this property that the hardening or setting of mortars and cements made from lime is due. *Mortar* consists of a mixture of slaked lime and sand: a gradual combination of the lime with the silica occurs, and this helps to harden the mixture. *Hydraulic mortars*, which harden under water, are prepared by carefully heating an impure lime containing clay and silica: a compound silicate of lime and alumina appears to be formed on moistening the powder, which then solidifies, and is unacted upon by water. Lime is largely used in agriculture, its action being, 1st, to destroy the excess of vegetable matter contained in the soil; and 2ndly, to liberate the potash for the use of the plants from heavy clay soils by decomposing the silicate.

Calcium Carbonate, or *Carbonate of Lime*, $CaCO_3$.—This salts occurs most widely diffused, as chalk, limestone, coral, and marble; many of those enormous deposits being made up of the microscopic remains of minute sea-animals. Calcium carbonate exists crystalline as calc-spar, or Iceland spar (rhombohedral or hexagonal system, Fig. 50 p. 181), and also in a different form, arragonite (rhombic, Fig. 55 p. 183); so that this substance is dimorphous. The carbonate is almost insoluble in pure water, but readily dissolves when the water contains carbonic acid, giving rise to what is termed *temporarily hard water*. Such a water deposits a crust of calcium carbonate on boiling, owing to the escape of the carbonic acid. The well-known evil of boiler crust is caused by these deposits. The formation of such a crust may be checked, if not avoided, by adding a small quantity of sal-ammoniac to the water, soluble calcium chloride and volatile ammonium carbonate being formed. Temporarily hard water may be softened by the addition of lime suspended in water, which unites with the carbonic acid present, forming insoluble calcium carbonate; the carbonic acid being thus removed, the calcium carbonate previously in solution is also precipitated. This is known as Clark's process of softening water.

Calcium Sulphate, $CaSO_4$.—This occurs in nature as a mineral termed *Anhydrite*, and combined with $2H_2O$ as selenite, gypsum, or alabaster. It is soluble in 400 parts of water, and is a very common impurity in spring water, giving rise to what is termed *permanent hardness*, as it cannot be removed by boiling. Gypsum when moderately heated loses its water and is then called plaster of Paris: this when moistened takes up two atoms of water again and sets to a solid mass, and is therefore much used for making casts and moulds.

Calcium Chloride, $CaCl_2$.—This soluble salt is formed when limestone or marble is dissolved in hydrochloric acid (see p.

80) : if the solution be then evaporated, colourless needle-shaped crystals of the hydrated chloride, $CaCl_2+6\ H_2O$, are formed. When these are dried, the substance still retains $2H_2O$, and forms a porous mass, which takes up moisture with great avidity, and is much used for drying gases. When this mass is more strongly heated, it fuses and parts with all its water.

Bleaching-Powder, or *Chloride of Lime*, $CaCl_2\ Ca(ClO)_2$ or $Ca\left\{\begin{matrix}Cl\\OCl,\end{matrix}\right.$ is obtained by the action of chlorine upon slaked lime (see p. 100).

$$3Ca(OH)_2 + 2Cl_2 = 2Ca\left\{\begin{matrix}Cl\\OCl\end{matrix}\right. + CaCl_2 + 2H_2O.$$

Chemists hold different views concerning the constitution of bleaching-powder; according to one view it is a compound of calcium chloride and calcium hypochlorite, as shown in the first formula; according to another it is regarded as a kind of double salt, represented by the second formula, the molecular weight being half that of the first.

If a clear solution of bleaching-powder be heated with a small quantity of oxide of cobalt or of copper, the oxygen of the bleaching-powder is gradually evolved and calcium chloride left behind.

Calcium Fluoride, or *Fluorspar*, CaF_2.—Found crystallized in cubes in Derbyshire and Cumberland. When heated with sulphuric acid, calcium sulphate and hydrofluoric acid (see p. 116) are formed. It is sometimes used as a flux in the reduction of metals, whence its name Fluorspar is derived.

Among the remaining compounds of calcium may be mentioned *Calcium phosphate*, or bone phosphate, $Ca_3(PO_4)_2$ (see p. 144), and the mineral apatite, $Ca_3(PO_4)_2 + Ca_2PO_4.F$, now largely used for making artificial manures; *Calcium sulphide*, CaS, an insoluble substance formed in the soda-ash process (see p. 195) : and *Calcium pentasulphide*, CaS_5, a soluble salt. The spectrum of calcium is a very peculiar one, containing a number of distinct bright lines, by which the presence of this metal can be easily ascertained. (See Chromolith No. 9.)

STRONTIUM.

Symbol Sr, *Atomic Weight* 87·2.

This element occurs in much smaller quantities than calcium, or even barium, being found in only a few mineral species, especially *strontianite* the carbonate, and *celestine* the sulphate. Strontium likewise occurs as chloride in minute quantities in certain spring waters. The metal has a yellowish-white colour, and is prepared by the electrolysis of the fused chloride. It resembles calcium closely in its properties; its specific gravity is 2·54. When heated in the air it burns, forming the monoxide strontia.

Strontium Monoxide, or *Strontia*, SrO.—This oxide is best obtained by decomposing the nitrate by heat: it unites with water, evolving great heat, and forming the *hydrate* $Sr(OH)_2 + 8H_2O$; this is soluble in water, and absorbs carbonic acid with avidity. The native salts of strontium, viz., the carbonate and sulphate, are insoluble, and serve for the preparation of the remaining salts. The *nitrate*, $Sr(NO_3)_2$, and the *chloride*, $SrCl_2$, are soluble in water: these are the only salts of this metal which are employed in the arts, being used for the preparation of red fires, as the soluble salts of strontium have the power of colouring the flame crimson. The spectrum of strontium is a very characteristic one (see Chromolith No. 10), and by this means the minutest trace of this substance can be easily and certainly detected, even in presence of calcium and barium salts.

BARIUM.

Symbol Ba, *Atomic Weight* 136·8.

Barium compounds occur somewhat more widely dispersed than those of strontium, the two most common barium minerals being the sulphate, or *heavy spar*, and the carbonate, or *witherite*. The metal barium has not yet been obtained in the coherent state, but the metallic powder may be prepared in a similar way to the two former metals, which it closely resembles in its properties.

Barium Monoxide, or *Baryta*, BaO.—The best way of forming this oxide is to decompose the nitrate by heat; it is a greyish porous mass, which fuses at a high temperature, and takes up water with evolution of much heat, forming a crystalline hydrate, $Ba(OH)_2 + 8H_2O$. This hydrate is soluble in twenty parts of cold water, and the solution on exposure to the air rapidly absorbs carbonic acid, and becomes milky.

Barium Dioxide, BaO_2.—When baryta is gently heated in a current of oxygen gas, the two substances combine together to form a dioxide containing twice as much oxygen as baryta: this additional atom of oxygen is, however, evolved at a higher temperature: and the proposal, made long ago, to use this decomposition for the manufacture of oxygen from the air has recently been successfully effected, and may be productive of valuable results in providing a cheap supply of pure oxygen. For this purpose, as soon as the dioxide BaO_2 has been reduced to BaO, the temperature is lowered, and air passed over the baryta; this again takes up oxygen, passing into BaO_2, which again is decomposed by a higher temperature (see p. 12). There are no salts known corresponding to this oxide.

Barium Chloride, $BaCl_2$.—This soluble salt is one of the most important compounds of barium: it crystallizes in flat scales containing two molecules of water. It may be prepared by dissolving the native carbonate in hydrochloric acid, and is largely used as a precipitant for sulphuric acid.

Barium Sulphate, $BaSO_4$, occurs native and crystalline as heavy spar; specific gravity 4·6 (whence the name Barium, from βαρύς, heavy). It is one of the most insoluble salts known, and falls as a white crystalline precipitate when any soluble barium salt is brought into a solution of a sulphate. It is used as a paint, and the precipitated salt is termed *blanc fixe*, whilst the native heavy spar, when ground, is largely used to adulterate white lead.

The other more important salts of barium are the *nitrate*, $Ba(NO_3)_2$, a soluble salt; the *sulphide*, BaS, obtained by heating heavy spar with coal, and decomposing on addition of water into hydroxide, $Ba(OH)_2$, and hydrosulphide, $Ba(SH)_2$, both of which dissolve in water; the *carbonate*, $BaCO_3$, an insoluble substance, occurring native as witherite: *Barium silicofluoride* and *phosphate* are insoluble salts, whilst strontium silicofluoride is soluble in water. The volatile salts of barium have the power of communicating a peculiar green colour to the flame, and the spectrum of barium contains a number of characteristic green lines, by means of which the presence of minute traces of this substance can be detected. (See Chromolith No. 11.)

CLASS III.—THE ZINC GROUP.

Beryllium, Magnesium, Zinc, Cadmium.

BERYLLIUM.

Symbol Be, *Atomic Weight* 9·03.

This rare metal is found in the mineral Beryl, Al_2O_3, 3BeO, $6SiO_2$. It is a light white metal (sp. gr. 2.1), closely resembling magnesium. It forms a monoxide, BeO, and yields a series of soluble, colourless salts, which have a characteristic sweetish taste, whence the name Glucinum, by which the element is sometimes designated.

MAGNESIUM.

Symbol Mg, *Atomic Weight* 24·3, *Specific Gravity* 1·74.

This element occurs in large quantities as carbonate, along with calcium carbonate, in *dolomite* or mountain limestone; and also in sea-water and certain mineral springs as chloride and sulphate. The metal is best obtained by heating magnesium chloride with metallic sodium, sodium chloride and metallic magnesium being formed. Magnesium is of a silver-white colour and has a specific gravity of 1·75, it fuses at a low red-heat: it is volatile and may be easily distilled at a bright red-heat; when soft it can be pressed into wire, and with care it may be cast like brass, although when strongly heated in the air it takes fire and burns with a dazzling white light, with the formation of its only oxide, magnesia. The light emitted by burning magnesium wire is distinguished for its richness in chemically active rays, and this substance is therefore employed as a substitute for sunlight in photography, and has been employed with success for photographing the interior of the Pyramids, caverns, &c.

Magnesium does not oxidize in dry air; it is only slowly acted upon by cold water, but more rapidly by hot water; it dissolves quickly in sulphuric and hydrochloric acids, with evolution of hydrogen.

Magnesium Oxide, or *Magnesia*, MgO.—A light white amorphous infusible powder, obtained by heating the carbonate or nitrate; it is largely used in medicine, and known as calcined magnesia. It unites with acids to form the magnesium salts, but it does not possess a strong alkaline reaction. The most important salts of magnesium are:—

Magnesium Chloride, $MgCl_2$, a fusible salt obtained by evaporating magnesia dissolved in hydrochloric acid with an equal quantity of sal-ammoniac; on fusion the latter salt volatilizes, and the magnesium chloride remains behind. It occurs in sea-water, and in certain salt-beds, *e.g.* those of Stassfurt, as *carnallite*, $MgCl_2 + KCl + 6H_2O$. Magnesium chloride is largely used as an anti-mildew in sizing cotton cloth.

Magnesium Sulphate, $MgSO_4 + 7H_2O$.—This is a soluble substance known as Epsom Salts; it occurs in a spring in Surrey, and also at Stassfurt as *kieserite*, $MgSO_4 + H_2O$; it is now largely made from dolomite by separating the lime with sulphuric acid. Magnesium sulphate forms, with the alkaline sulphates, double salts in which the alkaline sulphate takes the place of one of the seven molecules of the water of crystallization; thus $MgSO_4, K_2SO_4 + 6H_2O$ is the potash double salt.

Magnesium Carbonate, $MgCO_3$, is an insoluble compound, occurring as a crystallized mineral termed *magnesite*. The *magnesia alba* of the shops is a varying mixture of carbonate and hydroxide, made by precipitating a hot solution of magnesium sulphate with sodium carbonate. *Magnesium Sulphide*, MgS, is not formed in the wet way.

Magnesium resembles in many respects the metals of the alkaline earths, but it may be distinguished from these by the solubility of the carbonate in ammonium chloride, as well as by the ready solubility of the sulphate in water. Magnesium forms an insoluble double phosphate with ammonia,

$MgNH_4PO_4 + 6H_2O$; and it is in this form the metal is usually estimated.

ZINC.

Symbol Zn, *Atomic Weight* 65·1, *Specific Gravity* 6·8 to 7·2, *Vapour Density* 32·5.

Zinc is an abundant and useful metal, closely resembling magnesium in its chemical characters; but it is much more easily extracted from its ores than this latter metal. The chief ores of zinc are the sulphide or *blende*, the carbonate or *calamine*, and *red zinc ore.* In order to extract the metal, the powdered ore is roasted, *i.e.* exposed to air at a high temperature, so as to convert the sulphide or carbonate into oxide; the roasted ore is then mixed with fine coal or charcoal and strongly heated in crucibles or retorts of peculiar shape; the zinc oxide is reduced by the carbon, carbon monoxide comes off, and the metallic zinc distils over, and is easily condensed.

Zinc is a bluish-white metal, exhibiting crystalline structure: it is somewhat brittle at the ordinary temperature, but when heated to about 130°, it may be rolled out or hammered with ease, whilst if the temperature is raised to 200°, it is again brittle, and may be broken up in a mortar. Zinc melts at 423°, and at a bright red-heat it begins to boil, and volatilizes, or if air be present it takes fire and burns with a luminous greenish flame, forming zinc oxide. Zinc is not acted upon by moist or dry air, and hence it is largely used in the form of sheets, and is employed as a protecting covering for iron, which when thus coated is said to be *galvanized.* Zinc easily dissolves in dilute acids with evolution of hydrogen, and is therefore used as the oxidizable portion of the galvanic battery. Brass is a useful alloy of one part of zinc and two of copper; German silver is an alloy of zinc, nickel, and copper.

Zinc Oxide, ZnO, is the only known compound of this metal with oxygen, and is obtained by burning the metal, or by precipitating a soluble zinc salt with an alkali, and heating the precipitate. Zinc oxide is an insoluble white amorphous powder, which when heated becomes yellow but loses this colour on cooling; it dissolves easily in acids, giving rise to the zinc salts. It is used as a pigment, and termed zinc white.

The most important salts of zinc are:

Zinc Sulphate, $ZnSO_4 + 7H_2O$, a soluble salt, crystallizing in long prisms, and commonly called *white vitriol:* this salt is isomorphous with magnesium sulphate, and, like the latter salt, it forms a series of double salts with the sulphates of the alkali metals.

Zinc Chloride, $ZnCl_2$, a white soluble deliquescent substance, formed by burning zinc in chlorine; or, better, by dissolving the metal in hydrochloric acid. It is volatile at high temperatures and its vapour density has been found to be 67·8.

Zinc Sulphide, ZnS, occurs as a crystalline mineral called *blende*, generally coloured, from presence of iron and other impurities; it is obtained artificially as a white gelatinous precipitate, insoluble in acetic, but soluble in a mineral acid, when an alkaline sulphide is added to a soluble zinc salt.

Zinc Carbonate, $ZnCO_3$, an insoluble substance occurring native as calamine: it cannot be prepared by precipitating a solution of zinc salt by an alkaline carbonate, as a quantity of oxide is precipitated along with the carbonate.

The salts of zinc can be distinguished by the solubility of the hydroxide in excess of both potash and ammonia, by the white sulphide insoluble in acetic acid, and by the green colour which a solution of cobalt chloride imparts to zinc salts when heated before the blowpipe.

The vapour density of zinc is 32·5, or one half its atomic weight. Hence the molecule of zinc in the gaseous condition, unlike the greater number of elements, contains only one atom.

CADMIUM.

Symbol Cd, *Atomic Weight* 111·9, *Density of Vapour* 55·8.

This is a comparatively rare metal, occurring in small quantities in most zinc ores. In its chemical relations it closely resembles zinc. It is, however, more volatile than the latter metal, and therefore distils over first in the preparation of zinc. Cadmium is a white ductile metal having a specific gravity of 8·6, melting at 315° and boiling at 860°. It may be easily distinguished and separated from zinc as it yields a bright yellow sulphide insoluble both in alkaline sulphides and in hydrochloric acid. The metal takes fire when heated in the air, forming a brown *oxide*, CdO. The *chloride*, $CdCl_2$, and *sulphate*, $CdSO_4$, are soluble well-crystallizing salts. *Cadmium iodide*, CdI_2, is occasionally used in photography, and the yellow *sulphide*, CdS, has been employed as a pigment. The vapour density of cadmium is half its atomic weight; hence the molecule of cadmium gas, like that of zinc and mercury (see pp. 211, 223), contains one atom of the metal.

LESSON XXII

CLASS IV.—THE LEAD GROUP.—*Lead, Thallium*

LEAD

Symbol Pb (*Plumbum*), *Atomic Weight* 206·4, *Specific Gravity* 11·3

Lead only occurs free in nature in very minute quantities; all the lead of commerce is obtained from *galena*, or lead sulphide, PbS. The mode of reducing lead from this ore is a very simple one; the galena is roasted in a reverberatory furnace, with the addition of a small quantity of lime to form a fusible slag with any siliceous mineral matter present in the ore. By the action of the air a portion of the sulphide is oxidized to sulphate, whilst in another portion the sulphur burns off as sulphur dioxide, and lead oxide is left behind; after the lapse of a certain time the air is excluded and the heat of the furnace raised; the lead sulphate and oxide formed both decompose the remaining sulphide, giving off sulphur dioxide and leaving metallic lead behind:

$$(1)\ PbSO_4 + PbS = 2Pb + 2SO_2.$$
$$(2)\ 2PbO + PbS = 3Pb + SO_2.$$

Galena almost always contains a small quantity of silver, which is extracted by a process described on p. 225. Lead is a bluish-white coloured metal, and so soft that it may be scratched with the nail; it may be drawn out to wire, or hammered into plate, but possesses little tenacity or elasticity, and a wire 2 mm. in diameter breaks with a load of 2 kilos. Lead melts at 334°, and at a higher temperature volatilizes, though not in quantity sufficient to enable it to be distilled.

The bright surface of the metal remains permanent in dry air, but it soon becomes tarnished in moist air, owing to the formation of a film of oxide; and this oxidation proceeds rapidly in presence of a small quantity of weak acid, such as carbonic or acetic. In pure water freed from air lead also preserves its lustre; but if air be present, lead oxide is formed, and this dissolving slightly in the water a fresh portion of metal is exposed for oxidation. This solvent action of water upon lead is a matter of much importance, owing to the common use of lead water-pipes, and the peculiarly poisonous action of lead compounds upon the system when taken even in minute quantities for a length of time. The small quantity of certain salts contained in all spring and river waters exerts an important influence on the action of lead: thus waters containing nitrates or chlorides are liable to contamination with lead, whilst those hard waters containing sulphates or carbonates may generally be brought into contact with lead without danger, as a thin deposit of sulphate or carbonate is formed, which preserves the metal from further action. If the water contains much free carbonic acid, it should not be allowed to come into contact with lead, as the carbonate dissolves in water containing this substance. The presence of lead in water may easily be demonstrated by passing a current of sulphuretted hydrogen through a deep column of the acidified water, and noticing whether the liquid assumes a brown tinge owing to the formation of lead sulphide.

Three compounds of lead and oxygen are known:

1. *Lead Monoxide*, or *Litharge*, PbO, a straw-coloured powder, obtained by heating lead in a current of air, fuses at a red heat, solidifying to scaly crystals termed *litharge* or *massicot*. Lead oxide is soluble in caustic potash, and is

deposited from a hot solution in the form of rhombic prisms. This oxide forms with acids the important series of lead salts, which are generally colourless, the soluble ones acting as violent poisons. Lead oxide combines with silica to form an easily fusible silicate, or glass: thus earthen crucibles in which the oxide is fused are rapidly attacked. The white hydrated oxide $Pb(OH)_2$ is obtained by precipitating a soluble salt of lead by caustic potash, and this when heated yields the oxide.

2. *Lead Dioxide*, or *Puce-coloured Oxide*, PbO_2.—This oxide is a brown powder obtained by passing chlorine through the hydrated monoxide, or by digesting red lead with nitric acid. Lead dioxide does not form salts with acids. When heated it yields up half its oxygen; when acted upon with warm hydrochloric acid, chlorine is evolved, and lead chloride is formed.

3. *Red Oxide*, or *Red Lead*, a compound of the two last oxides, having the composition Pb_3O_4 or $2\ PbO + PbO_2$. It is obtained by exposing *massicot* to the air at a moderate red heat, oxygen being absorbed. Red lead is chiefly used in glass-making (see p. 231). When treated with dilute nitric acid the lead monoxide dissolves, forming soluble lead nitrate, leaving the puce-coloured oxide behind.

Lead Nitrate, $Pb(NO_3)_2$, is the most important of the soluble salts of lead. This compound is obtained by dissolving the oxide, the carbonate, or metallic lead in warm nitric acid; it crystallizes in octohedra, and dissolves in eight parts of cold water, and when heated strongly it yields red fumes of NO_2 (see p. 70).

Lead Acetate, or *Sugar of Lead*, is also a soluble salt, which will be described under Acetic Acid.

Almost all the other lead salts are insoluble in water. *Lead Carbonate*, $PbCO_3$, is found native as *cerusite*. *White lead*, so much used as a paint, is a compound of lead carbonate and lead hydroxide. This same compound is obtained in the pure state by precipitating a cold solution of the nitrate with an alkaline carbonate, when it falls down as a white powder. For preparing white lead in quantity two plans are employed —the one similar in principle to that by precipitation as above described; and the second an old and interesting process, known as the Dutch method. In this process thin sheets of lead are rolled into a coil, and each coil placed in an earthen pot containing a small quantity of crude vinegar (acetic acid); several hundreds of these jars and coils are packed on a floor in a bed of stable manure or spent tan-bark, and then covered with boards, whilst a second layer of pots similarly charged is placed above; and this is continued until the building is filled. After remaining thus for several weeks, the coils are taken out, when the greater part of the lead is found to be converted into white carbonate. It appears that, to begin with, a lead acetate is formed, and that the acetic acid is gradually driven out from its combination by the carbonic acid evolved from the putrefying organic matter, and thus enabled to unite with another portion of the lead lying underneath that which was first attacked. The composition of white lead varies somewhat, but it generally corresponds pretty closely with the formula $2\ PbCO_3 + Pb(OH)_2$.

Lead Sulphide, or *Galena*, PbS, is found native, and constitutes the chief ore of the metal. It is prepared as a black precipitate by passing sulphuretted hydrogen gas through a solution of a lead salt. Galena crystallizes in cubes and octohedra, and possesses a bright bluish-white metallic lustre.

Lead Sulphate, $PbSO_4$, is a white insoluble salt, which is found native, and is prepared artificially by adding sulphuric acid to a soluble lead salt.

Lead Chloride, $PbCl_2$, is prepared by adding hydrochloric acid to a strong solution of lead nitrate, when a crystalline precipitate of lead chloride is formed. It dissolves in about thirty parts of boiling water, separating out in shining needles on cooling.

Lead Iodide, PbI_2, is precipitated in the form of splendid yellow spangles, when hot solutions of potassium iodide and lead nitrate are mixed and allowed to cool.

Lead Chromate, $PbCrO_4$, is a yellow insoluble salt, used as a pigment under the name of *chrome yellow*.

The lead salts in general are isomorphous with those of the metals of the second class, and this analogy is further shown by the fact that the sulphates of lead and of barium are both insoluble in water. Hence it is usually assumed that lead is a dyad. We are, however, acquainted with a volatile compound of lead with an organic radical, viz., lead-ethyl,

$Pb(C_2H_5)_4$, whose vapour density is 162·5. This shows that lead is a tetrad element, at least that organic compounds contain one atom of tetrad lead. In the inorganic compounds, on the other hand, lead acts as a dyad, for the vapour-density (air = 1) of lead chloride has been found to be 9·6, corresponding to the molecular formula $PbCl_2$.

Lead can easily be recognised,—First, by the black sulphide, soluble in dilute nitric acid; secondly, by the white insoluble sulphate; thirdly, by the yellow iodide and chromate; and fourthly, by the easy reduction of the metal in the form of a malleable bead when any of the salts are heated before the blowpipe with a reducing agent.

THALLIUM.

Symbol Tl, *Atomic Weight* 203·6, *Specific Gravity* 11·85.

Thallium was discovered in 1861 by Mr. Crookes, by means of spectrum analysis, in the deposit in the flue of a pyrites burner (see p. 126). The presence of this new metal is indicated by the occurrence of a splendid green line in the spectrum (see Chromolith No. 5). Metallic thallium closely resembles lead in its physical properties; the freshly cut surface has a bluish-white lustre, which rapidly tarnishes; it is so soft that it receives impressions of the nail, and can be easily drawn into wire; it melts below a red-heat. It is found to occur in many specimens of iron pyrites, and appears to take the place of arsenic, which is a common impurity of this mineral. Metallic thallium undergoes gradual oxidation, so that it is best preserved in water; when strongly heated in oxygen, it takes fire, and burns with a bright green flame. Thallium dissolves easily in nitric and sulphuric acids with evolution of hydrogen, but more slowly in hydrochloric acid owing to the insolubility of the chloride. Two oxides of this metal are well characterised. *Thallium monoxide*, Tl_2O, and *Thallium Trioxide*, Tl_2O_3. Thallium monoxide corresponds in composition, and somewhat resembles in properties, the alkali potash, K_2O, as it is soluble in water, yielding an alkaline caustic solution, *thallium hydroxide*, $Tl(OH)$, which absorbs carbonic acid from the air, forms a well-defined series of salts termed the *thallious salts*, isomorphous with the corresponding potassium compounds. Of these the *sulphate*, Tl_2SO_4, and the *mono-chloride*, TlCl, are the most important. The sulphate is a soluble salt, crystallizing in six-sided prisms, and furnishing octohedral crystals of an alum with aluminium sulphate

$$Al_2(SO_4)_3 + Tl_2SO_4 + 24H_2O\,;$$

whilst the chloride is only slightly soluble in water, in this respect more nearly resembling the corresponding lead salt. *Thallium carbonate* Tl_2CO_3, is also a soluble salt, requiring about twenty-five parts of cold water for solution. The *sulphide*, Tl_2S, is an insoluble black powder, precipitated when an alkaline sulphide is added to any soluble thallium compound. A series of *thallic salts* exists corresponding to the trioxide : of these the *trichloride*, $TlCl_3$, is the most important.

The soluble thallium salts are colourless, and act as strong poisons ; the metal is precipitated in a pulverulent form when a piece of zinc is introduced into its solutions. It will be seen that the properties of thallium and its compounds are intermediate between those of lead and the alkalis.

Thallium can readily be detected by the insolubility of its sulphide, iodide, and chloride, in which it resembles lead, and by its soluble hydroxide, and insoluble platinum double salt, in which it resembles potash.

LESSON XXIII

CLASS V.—THE COPPER GROUP

Copper, Mercury, Silver

COPPER

Symbol Cu, *Atomic Weight* 63·1, *Specific Gravity* 8·93

Copper is an important metal, largely used in the arts, and has been known from very early times, as it occurs in the metallic or native state, and is moreover easily reduced from its ores. Metallic copper is found in considerable quantity in North America and other localities, crystallizing in cubic and octohedral forms; but the chief sources of copper are the following ores: (1) a compound of copper, sulphur, and iron known as *copper pyrites*, $Cu_2S + Fe_2S_3$: (2) cuprous sulphide, Cu_2S; (3) the carbonate or *malachite*, $CuCO_3 + CuH_2O_2$, or $Cu_2(OH)_2CO_3$; and (4) the red or cuprous oxide, Cu_2O. The Cornish mines yield large quantities of copper, whilst much ore is furnished by Chili and South Australia. Pure metallic copper can be obtained by reducing the oxide in a current of hydrogen gas, or by the electrolytic decomposition of a salt of copper.

Metallurgy of Copper.—The process for obtaining copper on a large scale from the carbonate or oxide is a very simple one, viz., merely reducing these ores together with carbon and some silica in a wind furnace. The reduction of the metal is more difficult when the commoner ore, copper pyrites, is employed. In this case the ore is repeatedly roasted, in order partially to convert the cuprous sulphide into oxide, and the roasted ore melted in a reverberatory furnace with the addition of sand or silicious slag : in this operation the cuprous oxide becomes converted into the corresponding sulphide, whilst the iron oxidizes and unites with the silica to form a light and fusible slag. The impure cuprous sulphide fuses and sinks to the lower portion of the furnace, forming the "mat" or coarse metal: and by repeating this operation a pure cuprous sulphide or "fine metal" is obtained. In order to prepare the metallic copper free from sulphur, this fine metal is roasted, and afterwards fused in contact with the air. During the first part of the operation a portion of the sulphur is burnt off, cupric oxide being formed; and in the latter stages of the process this oxide acts upon the remaining quantity of sulphide, forming sulphur dioxide and metallic copper:—

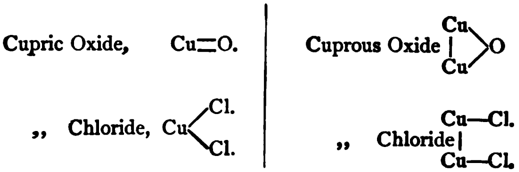
$$Cu_2S + 2CuO = SO_2 + 4Cu.$$

In order to get rid of the last traces of oxide, the molten copper is "poled" or stirred up with a piece of green wood.

Metallic copper possesses a peculiar deep red colour, which is best seen when a ray of light is several times reflected from a bright surface of the metal; it is very malleable and ductile, and possesses great tenacity, a wire of two mms. in diameter supporting a weight of 140 kilos.; it melts at a red-heat, and is slightly volatile at a white-heat, communicating a green tint to a flame of hydrogen gas, which is passed over it; and it is one of the best conductors of heat and electricity. Copper does not oxidize either in pure dry or moist air at ordinary temperatures, but if heated to redness in the air, it rapidly oxidizes to scales of copper oxide. Steam is not decomposed by metallic copper at a red-heat. Finely divided copper dissolves in hydrochloric acid with evolution of hydrogen; when heated with strong sulphuric acid, sulphur dioxide (p. 121) is evolved, and copper sulphate formed; and when acted upon with nitric acid, copper nitrate is produced, and nitric oxide (p. 68) liberated.

Alloys of Copper.—Many of the copper alloys are of importance. Brass is an alloy containing about two-thirds of copper and one-third of zinc; it is harder than copper and can be more easily worked: the addition of one to two per cent. of lead improves the quality of brass for most purposes. The yellow- or muntz-metal, used for the sheathing of ships, contains sixty per cent. of copper. Bronze, gun-metal, bell-metal, and speculum-metal are other alloys of copper and tin in varying quantities. They are all remarkable for the property of being hard and brittle when slowly cooled, but of becoming soft and malleable if they are cooled suddenly when red-hot by dipping into cold water.

Copper forms two series of compounds, the *cuprous* and the *cupric* salts. In the latter copper acts as a dyad, whilst in the former it appears to be a monad. A hypothesis has been largely accepted, which regards copper as a dyad in both series of compounds (see also p. 228). The graphical formulæ of the cupric and cuprous salts would then be as follows:



Cupric Compounds.

Copper Monoxide, *Cupric Oxide*, or *Black Oxide*, CuO.—This oxide is formed when copper is heated in the air or when copper nitrate is heated to redness: it yields the blue and green cupric salts, imparts a light green colour to glass, and it is used in the laboratory as a means of giving oxygen for the combustion of organic substances (see *Organic Chemistry*). Hydrated copper oxide, $Cu(OH)_2$, is obtained as a light blue precipitate when a caustic alkali is added to a cupric salt: when this is heated to 100°, it loses its water, and the anhydrous oxide falls as a black powder. Cupric oxide is soluble in acids, furnishing a series of salts which crystallize well. Of these the most important soluble compounds are:

Copper Sulphate, $CuSO_4 + 5H_2O$.—This salt is sometimes known as *blue vitriol*, and is largely manufactured by dissolving copper oxide (copper scales) in sulphuric acid. It crystallizes in large blue crystals belonging to the triclinic or asymmetric system (Fig. 60); when heated to redness, it loses all its water of crystallization, and forms a white powder, which again at a higher temperature decomposes, leaving copper oxide. Copper sulphate, or cupric sulphate, is employed in calico-printing, and in the manufacture of Scheele's green and Brunswick green, and other copper pigments. Cupric sulphate and the other copper salts give, with excess of ammonia, a deep-blue coloured solution, forming a remarkable compound, capable of crystallizing, having the composition $CuSO_4 + 4\ NH_3 + H_2O$. On heating this compound green cuprammonium sulphate is obtained, $CuSO_4 + 2NH_3$; this may be considered to be ammonium sulphate in which two atoms of hydrogen have been replaced by one atom of dyad copper; thus: $\left.\begin{matrix} NH_2Cu \\ NH_4 \end{matrix}\right\} SO_4$. Many similar copper compounds are known, and the production of this blue colour may be used as a test for the presence of copper.

Copper Nitrate, $Cu(NO_3)_2 + 6H_2O$, a very soluble salt, crystallizing in large blue prisms, is obtained by dissolving copper in nitric acid. *Copper chloride*, $CuCl_2$, is formed when copper is brought into chlorine gas, or when copper oxide is dissolved in hydrochloric acid; it forms green needle-shaped crystals, $CuCl_2 + 2H_2O$, soluble in water and alcohol. The alcoholic solution burns with a characteristic green flame.

The insoluble copper salts are: *Copper sulphide*, CuS, obtained as a black precipitate, when sulphuretted hydrogen gas is passed through an acidified solution of copper salt; *Copper carbonate*, $CuCO_3$, is not known in the pure state, as the green precipitate obtained by adding a solution of an alkaline carbonate to a copper salt always contains hydrated oxide, $CuCO_3 + Cu(OH)_2$, and is identical with the mineral malachite. The mineral chessylite possesses a somewhat similar composition, viz., $Cu_3(OH)_2(CO_3)_2$; *Copper arsenite*, $CuHAsO_3$, or Scheele's green, a bright green powder used as a pigment, and obtained by mixing solutions of sodium arsenite and copper sulphate.

Cuprous Compounds.

Cuprous Oxide, or *Red Oxide*, Cu_2O, occurs native in ruby-red octohedral crystals. It is artifically prepared by heating equivalent quantities of cupric oxide and copper filings, or by boiling a solution of copper sulphate and sugar, to which excess of caustic potash has been added: the sugar reduces the copper salt, and cuprous oxide is precipitated as a bright red powder. Cuprous oxide imparts to glass a splendid ruby-red colour; it forms colourless salts with acids, which rapidly absorb oxygen from the air, and pass into the corresponding cupric compounds. The most important of these salts is *cuprous chloride*, $CuCl$, a white solid substance obtained by dissolving a mixture of cupric oxide and metallic copper in hydrochloric acid: it is insoluble in water but its solution in hydrochloric acid or ammonia possesses the remarkable property of absorbing carbonic oxide gas.

Cuprous Hydride, CuH, is a yellow precipitate obtained by adding a solution of hypophosphorous acid to a warm solution of copper sulphate. This compound evolves hydrogen when heated, and takes fire when thrown into chlorine gas.

The copper salts may be detected—(1) by the black insoluble sulphide: (2) by the blue hydroxide turning black on heating; (3) by the deep blue coloration with ammonia: (4) by the deposition of red metallic copper upon a bright surface of iron placed in the solution:

$$CuSO_4 + Fe = Cu + FeSO_4.$$

MERCURY.

Symbol Hg (*Hydrargyrum*), *Atomic Weight* 199·8, *Specific Gravity* at 0° 13·596, *Vapour Density* 99·9.

Mercury occurs in the native state, but the chief ore of mercury is the sulphide, or *cinnabar*, which occurs at Almaden in Spain, at Idria in Illyria, in California, and also in China and Japan. The metal is easily obtained by roasting the ore, when the sulphur burns off as the dioxide, and the metal volatilizes, and its vapour is condensed in earthen pipes.

Mercury is the only metal liquid at the ordinary temperature; it freezes at − 40°, crystallizing in octahedra; in the solid state it is malleable, and possesses a specific gravity of 14·0. It boils at 350° (measured by the air thermometer), and gives off a slight amount of vapour at the ordinary temperature. The density of its vapour when air = 1, is 6·697, and its vapour is 100 times as heavy as hydrogen. Hence its vapour density, like that of zinc and cadmium, is one half the atomic weight, and the molecules of mercury are monatomic. Mercury when pure does not tarnish in moist or dry air, but when heated above 350° it slowly absorbs oxygen, passing into the red oxide ; and it combines directly with chlorine, bromine, iodine, and sulphur. Hydrochloric acid does not attack mercury ; sulphuric acid, on heating, forms sulphur dioxide (p. 68) and mercuric sulphate; and nitric acid evolves nitric oxide, and forms mercurous or mercuric nitrate. Mercury is largely used in the processes of extracting gold and silver from their ores (pp. 225 and 260), and in the arts for silvering mirrors and other purposes. Mercury is deposited from its solutions upon metallic iron or copper, in the form of a grey powder, which becomes bright on burnishing. Mercury and its salts act as valuable medicines.

Mercury is a dyad, and, like copper, forms two oxides, HgO and Hg_2O, yielding two series of compounds, the *mercuric* and *mercurous* salts.

Mercuric Compounds.

Mercury Monoxide, or *Mercuric Oxide*, HgO, is obtained by moderately heating the nitrate, or by heating the metal in the air for some time at a temperature of 300°. The oxide thus prepared appears as a red crystalline powder : by precipitating it from a solution of the nitrate by caustic potash it falls as an amorphous yellow powder.

Mercuric Nitrate, $Hg(NO_3)_2$, is formed by the action of excess of nitric acid upon mercury, or the oxide.

Mercuric Chloride, or *Corrosive Sublimate*, $HgCl_2$, is prepared on a large scale by heating an intimate mixture of equal parts of mercuric sulphate, $HgSO_4$, and common salt :

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

It is also formed when mercury burns in chlorine. It acts as a violent poison ; it is soluble in water, crystallizing in rectangular octohedra : it fuses at 265°, and boils at 295°.

When ammonia is added to a solution of mercuric chloride, the so-called *white precipitate*, which is a chloride of mercury-ammonium, NH_2HgCl, is thrown down:

$$2NH_3 + HgCl_2 = NH_2HgCl + NH_4Cl.$$

Mercuric Sulphide, *Cinnabar* or *Vermilion*, HgS, occurs native, and may be prepared artificially by heating a mixture of sulphur and mercury. When precipitated from a solution of mercuric salt by sulphuretted hydrogen, the sulphide falls as a black amorphous powder, but on sublimation it becomes red and crystalline.

Mercurous Compounds.

The most important of these compounds is

Mercurous Chloride, or *Calomel*, $HgCl$.—It is generally prepared by heating a mixture of three parts of finely-divided metallic mercury with four parts of corrosive sublimate; the metal combines with half the chlorine of the corrosive sublimate, two molecules of calomel being formed,

$$HgCl_2 + Hg = 2HgCl.$$

The calomel sublimes, and is deposited in a solid cake: it must be finely ground and well washed, in order to free it from any soluble mercuric chloride which may remain undecomposed. Calomel is a white powder, insoluble in water; it is decomposed by potash and turned black by ammonia. It is used largely in medicine.

Mercurous Oxide, Hg_2O, is obtained as a black powder by digesting calomel with excess of caustic potash. On exposure to light, or when heated to 100°, it decomposes into mercury and mercuric oxide.

Mercurous Nitrate, $HgNO_3$, is prepared by acting with dilute nitric acid upon an excess of mercury.

The mercury compounds can be readily recognised—(1) by precipitation of black mercuric sulphide, insoluble in nitric acid; (2) by the reduction of liquid globules of the metal when any compound is strongly heated with sodium carbonate in a small tube; (3) by the deposit of metallic mercury on copper. The mercurous salts are distinguished by precipitating calomel when a chloride is added to a soluble salt; whilst the mercuric salts may be detected by the formation of red mercuric iodide, HgI_2.

SILVER.

Symbol Ag, *Atomic Weight* 107·66, *Specific Gravity* 10·5.

Silver was known to the ancients. It is found in the native state, as well as combined with sulphur, antimony, chlorine, and bromine. It is also contained in small quantities in galena (p. 212); and it can be extracted with profit from the lead prepared from this ore, even when the lead contains only two or three ounces of silver to the ton. The method thus adopted for the extraction of the silver depends upon the fact that the whole of the silver can be concentrated into a small portion of lead, by crystallization; metallic lead free from silver separates out in crystals, and a rich alloy is left. When the latter reaches the concentration of 300 oz. silver to the ton it is subjected to the operation of *cupellation*, in which the mixture is melted in a furnace on a porous bed of bone-earth, and a blast of air blown over the surface: the lead oxidizes, and the oxide (litharge) fuses, and partly runs away and partly sinks into the porous bed of the furnace, whilst the silver remains behind in the metallic state.

For the extraction of silver from the other ores, a process termed amalgamation is employed, in which mercury is used to dissolve the metallic silver. The argentiferous ores of Germany, in which the silver occurs in combination with sulphur, are worked in a different manner. The ore is roasted in a furnace with common salt, by which means the silver sulphide is converted into chloride: the mixture is then placed in casks which can be made to revolve, and scrap-iron and water added. The iron reduces the silver to the metallic state; and when this is fully accomplished, metallic mercury is added: this forms a liquid amalgam with the silver (and gold if any be present); and by distilling the mercury off, the silver is obtained in an impure state. A somewhat different method is employed in South America, where fuel is expensive. Silver possesses a bright white colour and a brilliant lustre, which it does not lose in pure air at any temperature; but when melted in the air it possesses the singular power of absorbing mechanically a large volume (twenty-two times its bulk) of oxygen: this gas it again gives out on solidifying—a phenomenon technically known as the "spitting" of silver.

Silver is the best conductor of heat and electricity known, and is extremely ductile; one gram of metal can be drawn out into a wire of 2,600 meters in length. Sulphur combines at once with silver, forming a black sulphide: silver articles long exposed to the air tarnish from this cause, the sulphur being derived from the small quantity of sulphuretted hydrogen contained in the air. Silver is easily soluble in nitric acid, the nitrate being formed and nitric oxide gas evolved; it also dissolves in hot sulphuric acid with formation of the sulphate and liberation of sulphur dioxide. This reaction is used for separating silver from gold (termed *parting*), the latter metal not being attacked by sulphuric acid.

Alloys of Silver.—Silver itself is largely used in the pure state for various purposes in the arts, but it is usually alloyed with a small quantity of copper when employed as coin or for articles of plate. The English coinage contains 7·5 per cent. of copper in the standard silver, whilst the French contains 10 per cent.

Compounds of Silver.

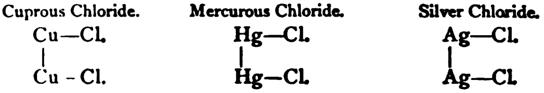
Silver forms two compounds with oxygen. The first, a strong base termed *Silver monoxide*, Ag_2O, is obtained in the form of a brown precipitate when caustic potash is added to a solution of silver nitrate. From this oxide, which is decomposed into metal and oxygen on heating, the ordinary silver salts may be derived by dissolving it in acids. The second oxide is called *Silver dioxide*, Ag_2O_2, and is obtained as a black powder by the action of ozone on metallic silver.

Silver Nitrate, $AgNO_3$, is the most important soluble salt of silver. Is is obtained in the form of large transparent tabular crystals on evaporating a solution of silver in nitric acid, and is soluble in its own weight of cold- and half its weight of hot-water, and in four parts of alcohol. Silver nitrate fuses easily on heating, and when cast into sticks goes by the name of *lunar caustic.* This salt undergoes decomposition when exposed to the sunlight in contact with organic matter, and a black substance, of unknown constitution, is formed : hence it is employed in the manufacture of an indelible ink for marking linen and other fabrics.

Silver Chloride, $AgCl$, is the most important of the insoluble salts. This salt occurs in nature, and is then known as *horn silver*, and is precipitated as a white curdy mass when solutions of a chloride and a silver salt are brought together. When exposed to sun- or day-light, the white chloride assumes a purple tint, which increases in depth as the action of light continues. This coloration arises from a partial decomposition of the salt, a small quantity of argentous chloride and free hydrochloric acid being formed. In presence of organic matter this change takes place much more rapidly; and upon this fact the phenomena of photography depend. Silver chloride fuses at about 260°, and at higher temperatures volatilizes; it is easily reduced to metallic silver in presence of zinc and sulphuric acid. The chloride is perfectly insoluble in pure water, but it dissolves appreciably in strong hydrochloric acid and in a solution of common salt, whilst it dissolves easily in ammonia : it is also readily soluble in a solution of sodium thiosulphate (p. 129) : and it is for this reason that the latter salt is used for "fixing" photographic pictures—that is, dissolving out the unaltered silver salt, and thus rendering the image permanent.

Silver Bromide, $AgBr$, falls as a white precipitate, when silver nitrate is added to an alkaline bromide; it is also acted upon by the light, and is soluble in ammonia and alkaline thiosulphates. *Silver Iodide*, AgI, is a yellow powder insoluble in water and ammonia, but dissolved by alkaline thiosulphates. *Silver Sulphide*, Ag_2S, occurs native in cubic crystals, as *silver glance;* is is precipitated as a black powder by passing sulphuretted hydrogen through solutions of salts of silver.

It will be seen that the silver salts are in every respect analogous to the cuprous and mercurous salts, and that in all of them the metals acts as monads. As mentioned on p. 220, a hypothesis has been largely accepted that in all these salts the formulæ given above must be doubled, and that the metals act in reality as dyads, as will be seen from the following formulæ :



Cuprous Chloride.

$$\begin{array}{l} Cu{-}Cl \\ | \\ Cu{-}Cl \end{array}$$

Mercurous Chloride.

$$\begin{array}{l} Hg{-}Cl \\ | \\ Hg{-}Cl \end{array}$$

Silver Chloride.

$$\begin{array}{l} Ag{-}Cl \\ | \\ Ag{-}Cl \end{array}$$

This hypothesis has been to some extent confirmed by the determination of the vapour density of cuprous chloride, whereas the vapour density of mercurous chloride agrees with the simpler formula. The latter may, however, be in reality due to the fact that in volatilization mercurous chloride splits up into mercuric chloride and mercury. Nevertheless until more satisfactory proofs of the hypothesis are obtained it is preferable to use the simpler formulæ.

Silver can be easily detected when in solution by the precipitation of the white curdy chloride on addition of hydrochloric acid or a soluble chloride, insoluble in water and nitric acid, and soluble in ammonia : the metal can be easily obtained in malleable globules before the blowpipe, whilst it is reduced from its solutions by metallic iron, copper, and mercury. Silver is estimated quantitatively either as the chloride or as the metal.

ELECTROTYPE PROCESS.

A firm bright deposit of such metals as silver, gold, copper, nickel, &c., can be obtained upon other metals or upon conducting surfaces by means of an electric current, the metal being deposited upon the negative pole. In the case of silver, the depositing solution is cyanide of silver dissolved in cyanide of potassium.

CLASS VI.—Contains the following Rare Metals :—

Yttrium, *Erbium*, *Cerium*, *Lanthanum*, *Didymium*, *Terbium*, *Ytterbium*, *Scandium*, *Samarium*.

These metals are chiefly found in minerals occurring in Scandinavia and the United States, of which the most important are *gadolinite*, *cerite*, *orthite*, and *samarskite*. The metals cerium, lanthanum, and didymium have been isolated ; they are malleable, and possess an iron-grey colour. All the members of the group form basic sesquioxides, and their sulphates combine with potassium sulphate to form double salts such as $Ce_2(SO_4)_3.K_2SO_4$.

CLASS VII.—THE ALUMINIUM GROUP.

Aluminium, *Gallium*, *Indium*.

ALUMINIUM.

Symbol Al, *Atomic Weight* 27·0, *Specific Gravity* 2·6.

This metal occurs in large quantities combined with silicon and oxygen in felspar and all the older rocks, and also in clay, marl, slate, and in many crystalline minerals. Metallic aluminium is obtained by the action of sodium at a high temperature on the double chloride of sodium and aluminium, and also by electrolysis. It is now manufactured on a large scale, and from its lightness (specific gravity 2·6) and its bright lustre, it has been used for the metallic portions of optical instruments as well as for ornamental work.

Alumina, Al_2O_3 ; *Specific Gravity* 3·9.—This is the only oxide of aluminium known. It occurs native in a nearly pure and crystalline state as *corundum*, *ruby*, *sapphire*, and in a less pure state as *emery*. Alumina is prepared by adding ammonia to a solution of alum ; a white precipitate of the *hydroxide*, $Al(OH)_3$, falls down, and this on being heated yields a white amorphous powder of pure alumina. This latter substance is attacked with difficulty by acids, but the hydroxide is easily soluble in acids and in the fixed caustic alkalis. Alumina acts as a weak base : the commonest aluminium salts are the alums, and their solutions have an acid reaction.

Alumina is largely used in dyeing and calico-printing as a mordant, as it has the power of forming insoluble compounds called *lakes* with vegetable colouring matter, and thus renders the colour permanent by fixing it in the pores of the cloth so that it cannot be washed out: such colours are termed *fast*.

Aluminium Chloride, $AlCl_3$, is a volatile white solid body, obtained by heating a mixture of alumina and charcoal in a current of chlorine gas; it is used in the manufacture of the metal. The vapour density of this compound is found to correspond to the molecular formula $AlCl_3$.

Aluminium Sulphate, $Al_2(SO_4)_3$, is a soluble salt prepared on a large scale for the use of the dyer by decomposing clay, by acting upon it with sulphuric acid: the solid mixture of silica and aluminium sulphate thus obtained goes by the name of alum-cake. The most useful compounds of alumina are, however, the alums, a series of double salts, which aluminium sulphate forms with the alkaline sulphates. *Potash alum*, or *Aluminium potassium sulphate*, has the composition $Al_2(SO_4)_3 + K_2SO_4 + 24H_2O$, and crystallizes in regular octahedra (Fig. 45). It may be prepared by dissolving the two sulphates together, and allowing the compound salt to crystallize, but it is usually obtained from the decomposition of a shale or clay containing iron pyrites, FeS_2: this substance gradually undergoes oxidation when the shale is roasted, absorbs oxygen from the air, and produces sulphuric acid, which unites with the alumina of the clay, and, on the addition of a potassium compound, alum crystallizes out.

Ammonia alum is a salt containing ammonium instead of potassium, $Al_2(SO_4)_3 + (NH_4)_2SO_4 + 24H_2O$; it is prepared on a large scale, the ammonia liquor of the gasworks, together with sulphuric acid, being added to the burnt shale instead of a potassium salt.

A large number of other alums are known, in which the isomorphous sesquioxides of iron, chromium, and manganese are substituted for the alumina in common alum: all these alums occur in octahedra, and cannot be separated by crystallization when present in solution together.

Clay is an aluminium silicate resulting from the disintegration and decomposition of felspar by the action of air and water, the soluble alkali being washed away. The formula of felspar is $AlKSi_3O_8$, or $Al_3O_3,K_2O.6SiO_2$. Kaolin or porcelain clay is the purest form of disintegrated felspar, containing no iron or other impurities. There are many very beautifully crystalline minerals, consisting of aluminium silicates combined with silicates of the metals of the alkalis and alkaline earths : amongst others, garnet, idocrase, mica, lepidolite, &c. Some silicates, such as stilbite, analcime, &c., retain water of crystallization, and are termed *zeolites.*

Aluminium salts can be detected when in solution by giving with ammonia a white precipitate, insoluble in excess, but soluble in caustic soda : the solid compounds assume a blue colour when moistened with cobalt solution and heated before the blow-pipe.

GLASS, PORCELAIN, AND EARTHENWARE.

The silicates of the alkali-metals are, as we have seen, soluble in water and non-crystalline ; those of the alkaline earths are soluble in acid and crystalline ; whilst compounds of the two are insoluble in water and acids, and do not assume a crystalline form. Such a compound when fused is termed a *glass.* There are four different descriptions of glass used in the arts, differing in their chemical composition and exhibiting corresponding differences in their properties :

(1) *Crown-* or *window-* and *plate-glass,* composed of silicates of sodium and calcium.
(2) *Bohemian glass,* consisting of silicates of potassium and calcium.
(3) *Flint glass* or *crystal,* containing silicates of potassium and lead ; and
(4) *Common green bottle-glass,* composed of silicates of sodium, calcium, iron, and aluminium.

The first and third of these kinds of glass are easily fusible, whilst the second or potash glass is much more infusible : the addition of oxide of lead increases the specific gravity and the lustre of the glass, as well as its fusibility. The common glass articles for household use are generally made of flint glass, whilst for chemical apparatus a soda-lime-glass is to be preferred. The potash-lime-glass is much employed where a difficultly fusible or hard glass is needed, as for instance in the manufacture of combustion tubes for organic analysis (see *Organic Chemistry*). The fourth description of glass is an impure mixture of various silicates, employed for purposes in which the colour and fineness of the glass is not of consequence.

In the preparation of all the fine qualities of glass, great care is requisite in the selection of pure materials, as well as in the processes of manufacture: generally the materials are melted together with a quarter to half their weight of "cullet" or broken glass of the same kind. After the glass articles have been blown or cast, they must be exposed to the process of "annealing," or slow cooling; otherwise they are so brittle as to be perfectly useless, breaking with the slightest touch, owing to the irregular contraction of the different parts brought about by rapid cooling. The following table shows the composition of the chief varieties of glass.

Ingredients for various Glasses.

Crown Glass.			*Bohemian Glass.*		
Quartz Sand	100	parts.	Pure Sand	100	parts.
Mild Lime	36	,,	Pure Pearlash . . .	60	,,
Soda Ash	24	,,	Chalk	8	,,
Sodium Sulphate . .	12	,,	Cullet	40	,,
Arsenic Trioxide . .	$\frac{1}{3}$	,,	Manganese Dioxide .	$\frac{3}{4}$	,,
Cullet	100	,,			

Mirror Plate.			*Flint Glass.*		
Pure Sand	100	parts.	Pure Sand	100	parts.
Soda Ash	35	,,	Red Lead	20	,,
Mild Lime	5	,,	Pearlash	40	,,
Arsenic Trioxide . .	$\frac{1}{6}$	,,	Nitre	2	,,
Cullet	100	,,	Cullet	50 to 100	,,

Coloured Glass.—Certain metallic oxides possess the power of colouring glass, when they are added in small quantity. Thus ferrous oxide produces a deep green colour (bottle-glass), whilst the oxides of manganese impart a purple tint to glass. These facts are made use of in the preparation of colourless glass; for as it is difficult to obtain materials perfectly free from ferrous oxide, which imparts a deep green colour, a small quantity of manganese dioxide is added to the mixture; this oxidizes the iron to ferric oxide which gives to glass a faint yellow tint, and this, in combination with the violet colour imparted by the manganese, gives rise to a nearly colourless glass. The addition of arsenic trioxide and nitre effects the same end. The colours of precious stones are imitated by adding certain oxides to a brilliant lead glass called "paste": thus the blue of the sapphire is given by a small quantity of cobalt oxide, whilst cuprous oxide imparts a ruby-red colour, and ferric oxide a yellow colour resembling topaz.

Porcelain and Earthenware.—The various forms of porcelain and earthenware consist of silicate of aluminium, in fact clay, in a more or less pure state, covered with some substance which fuses at a high temperature, and forms a glaze, giving a smooth surface and binding the material together, and thus counteracting the porous nature of the baked clay. For the manufacture of porcelain the finest white or China clay is used, resulting from the gradual decomposition of felspar, whilst for the common earthenware a coloured clay may be employed. The glaze used for porcelain is generally finely powdered felspar, the biscuit or porous ware being dipped into a vessel containing this substance suspended in water, and then strongly fired. The articles thus coated can be used for chemical purposes, as this glaze withstands the action of acids. For earthenware the so-called "salt glaze" is used. The mode of obtaining this glaze consists in throwing some common salt into the furnaces containing the strongly heated ware, when the salt is volatilized and undergoes decomposition on the heated surface, causing a deposit of a fusible silicate upon it, and rendering the ware impervious to moisture.

GALLIUM.

Symbol G, *Atomic Weight* 69·8.

This metal was discovered in 1876 by M. de Boisbaudran in certain zinc ores found in the Pyrenees. When held in a non-luminous gas flame, it yields a characteristic spectrum, consisting of two bright bands in the blue and violet, not far from the bands of indium. A remarkable property of this metal is its low melting-point, as it fuses at 30°. In its general properties this metal stands between aluminium and indium, and is identical with Mendeléeff's ekaluminium (p. 266).

INDIUM.

Symbol In, *Atomic* 113·4.

A metal discovered in 1863 by Messrs. Reich and Richter, by means of spectrum analysis in certain zinc ores. Its compounds impart a blue colour to flame, and its spectrum is characterised by two fine indigo-coloured lines, seen in No. 6 of the Chromolith. Indium is a soft white metal resembling cadmium in its appearance. It melts at 176°, and forms a sesquioxide, In_2O_3, and a chloride, $InCl_3$, in these respects resembling aluminium.

LESSON XXIV

CLASS VIII.—THE IRON GROUP

Manganese, Iron, Cobalt, Nickel, Chromium, Uranium

MANGANESE

Symbol Mn, *Atomic Weight* 55·0, *Specific Gravity* 8·0

Manganese occurs in nature as an oxide, and it can be obtained, though with difficulty, in the metallic state by heating the oxide very strongly with charcoal. The metal is of a reddish-white colour; it is brittle, and hard enough to scratch glass. It decomposes water at the ordinary temperature, with evolution of hydrogen; it cannot be preserved in the air without undergoing oxidation, and must be kept under naphtha, or in a sealed tube; it is slightly magnetic, and like iron, combines with carbon and silicon. Metallic manganese is not used in the arts, but an alloy of this metal and iron is now made on a large scale, and used in the manufacture of steel. Some of its oxides are used for the purpose of evolving chlorine from hydrochloric acid, and also for tinting glass a purple colour.

Manganese forms several well-characterised oxides.

(1) *Manganous oxide*, or *manganese monoxide*, MnO, is a basic body, furnishing the series of well-known manganous salts, in which the oxygen is replaced by its equivalent of another element, or an acid radical: thus MnO, $MnCl_2$, $MnSO_4$, $Mn(NO_3)_2$.

(2) *Manganic oxide*, or *manganese sesquioxide*, Mn_2O_3, which also forms salts, but of a much less stable character, and occurs in nature as the mineral braunite.

(3) *Red*, or *mangano-manganic oxide*, Mn_3O_4, a neutral body, corresponding to the magnetic oxide of iron, and occurring in nature as hausmannite.

(4) *Black oxide*, or *manganese dioxide*, MnO_2, a neutral substance, occurring as the ore of manganese in the minerals pyrolusite and varvacite.

(5) *Manganese trioxide*, MnO_3, which is an extremely unstable substance.

(6) *Manganese heptoxide*, Mn_2O_7, a dark green heavy liquid, obtained by the action of strong cold sulphuric acid upon potassium permanganate.

Manganese Monoxide, MnO, is a greenish powder, obtained by heating the carbonate in absence of air; it forms with acids a series of pink-coloured salts, and rapidly absorbs oxygen, passing into a higher state of oxidation. The hydroxide is precipitated as a white gelatinous mass, when an alkali is added to a solution of a manganous salt; this, however, rapidly becomes brown, owing to absorption of oxygen. Of the *manganous salts*, the chief soluble ones are, the *sulphate*, $MnSO_4 + 5H_2O$, a pink-coloured crystalline salt, prepared by acting on the dioxide with sulphuric acid, oxygen gas being evolved—

$$MnO_2 + H_2SO_4 = MnSO_4 + O + H_2O,$$

and the *chloride*, $MnCl_2 + 4H_2O$, a salt obtained by crystallization from the residues in the manufacture of chlorine from the dioxide and hydrochloric acid.

Among the insoluble manganous compounds of importance are the *sulphide*, MnS, obtained as a flesh-coloured precipitate by the addition of an alkaline sulphide to a soluble manganous salt, and the *carbonate* $MnCO_3$, which occurs native, crystallizing like calc-spar in rhombohedra, and prepared as a white powder by precipitating a manganous salt with an alkaline carbonate.

Manganese Sesquioxide, Mn_2O_3, exists in nature as *braunite*, and may be prepared artificially by exposing manganous oxide to a red heat. It forms a series of somewhat unstable salts, of which the manganese alum is one of the most interesting, being isomorphous with common alum, and in which Mn_2O_3 is substituted for Al_2O_3.

Manganese Dioxide, MnO_2, is the common black ore of manganese, and is termed *pyrolusite* by mineralogists; it can be artificially formed by adding a solution of bleaching powder to a manganous salt. This substance yields one-third of its oxygen when heated to redness (see p. 12), forming the red oxide, $3MnO_2 = Mn_3O_4 + O_2$, and gives up half its oxygen when heated with sulphuric acid (see above). It is largely used for the manufacture of chlorine, and is precipitated as a black hydrated powder by adding an alkaline hypochlorite to a manganous salt:

$$NaClO + 2NaOH + MnSO_4 = NaCl + Na_2SO_4 + MnO_2 + H_2O.$$

A somewhat similar reaction is now made use of to regain manganese dioxide from the manganese liquors of the chlorine stills; for this purpose the acid chloride of manganese solution is neutralized by limestone, and then a blast of air and steam blown through a mixture of the solution with milk of lime. Manganous hydroxide is first formed, and then combines with oxygen forming the dioxide. This is known as Weldon's process.

Manganese trioxide, MnO_3, is obtained by allowing a solution of potassium permanganate in sulphuric acid to drop on to sodium carbonate. It is a reddish amorphous deliquescent mass, which rapidly decomposes above 0°.

Manganic and Permanganic Acids.—When an oxide of manganese is fused in the air with caustic alkali, a bright green mass is formed which yields a dark green solution:

this contains *potassium manganate*, K_2MnO_4, which may be crystallized, and is isomorphous with potassium sulphate and chromate. If this green solution be allowed to stand, it slowly changes to a bright purple colour, and hydrated manganese dioxide is deposited,—hence its common name of mineral chameleon: it then contains a new salt in solution, viz. *potassium permanganate*, $KMnO_4$, which may be obtained in the crystalline state by evaporation, and is isomorphous with potassium perchlorate. The presence of a few drops of acid at once effects this decomposition of the green solution. On adding strong well-cooled sulphuric acid to potassium permanganate, a deep green heavy liquid is formed; this substance is *Manganese Heptoxide*, Mn_2O_7. It is easily decomposed on heating, evolving oxygen, and as this oxygen contains much ozone, an easy method to prepare ozonised air is to pour strong sulphuric acid upon potassium permanganate.

The manganates and permanganates readily give up a part of their oxygen in presence of organic matter, and they are now largely used as disinfectants, and known as Condy's liquids, as well as being employed in the laboratory for the purposes of volumetric analysis.

Manganese is chiefly characterised by the flesh-coloured sulphide, and by the formation of the green sodium manganate—a most delicate reaction.

IRON.

Symbol Fe, *Atomic Weight* 55·9, *Specific Gravity* 7·8.

Iron is of all metals the most important to mankind. The uses of iron were long unknown to the human race, the age of iron implements being preceded by those of bronze and stone. Pure metallic iron exists only in very small quantity on the earth's surface, almost entirely occurring in those peculiar structures known as meteoric stones, which have an extraterrestrial origin. The process of obtaining iron from its ores is a somewhat difficult one, and requires an amount of knowledge and skill which the early races of men did not possess.

The iron of commerce exists in three distinct forms, exhibiting very different properties, and possessing different chemical constitutions: 1, *wrought iron*; 2, *cast iron*; 3, *steel*. The first is nearly pure iron, the second is a compound of iron with varying quantities of carbon and silicon, and the third a compound of iron with less carbon than that needed to form cast iron. The modes of manufacture of these three kinds of iron are essentially different, and will be best understood when the properties of the metal have been described.

Pure iron in the form of powder may be obtained by the reduction of the oxide at a moderate heat in a current of hydrogen: it must, however, be retained in an atmosphere of hydrogen, as finely-divided iron takes fire and burns to oxide when exposed to the air. A button of pure iron may be prepared by exposing fine iron wire mixed with some oxide of iron to a very high temperature in a covered crucible, the oxide retaining the traces of impurity which the wire contained. Iron has a bright white colour, and, though soft, is remarkably tough, an iron wire two mm. in thickness not breaking until weighted with 250 kilos. The pure metal crystallizes in cubes: iron which has been uniformly hammered exhibits, when broken, a granular and crystalline structure: this structure, however, becomes fibrous when the iron is rolled into bars, and the more or less perfect form of the fibre determines to a great extent the value of the metal. This fibrous texture of hammered bar iron undergoes a change when exposed to long-continued vibration, the iron returning to its original crystalline condition; and many accidents have occurred in the sudden snapping of railway axles, owing to this change from the fibrous to the granular texture. Wrought iron melts at a very high temperature: but as it becomes soft at a much lower point, it can be easily worked, especially as, when hot, it possesses the peculiar property of "welding"; that is, the power of uniting firmly when two clean surfaces of hot metal are hammered together.

Iron and certain of its compounds are strongly magnetic, but the metal loses this power when red-hot, regaining it upon cooling. Contact with a magnet induces temporary magnetism in a bar of pure iron, but a bar of steel becomes permanently magnetic under the same circumstances, and its magnetism may be strengthened by rubbing it with a stronger magnet. A solid mass of iron does not oxidize or tarnish in dry air, at the ordinary temperature, although iron powder takes fire spontaneously; but if heated it oxidizes, with the production of black scales of oxide, and when more strongly heated in the air, or plunged into oxygen gas, it burns, with the formation of the same black oxide. In pure water iron does not lose its brilliancy; but if a trace of carbonic acid is present, and access of air is permitted, the iron begins at once to oxidize at the surface, or to rust, forming a hydrated sesquioxide. Iron decomposes steam at a red-heat, liberating hydrogen (see p. 19), and forming the black oxide produced by the combustion of iron in oxygen.

Iron forms two basic oxides, both of which give rise to well-marked series of compounds: (1) *Ferrous oxide*, FeO, giving rise to the *Ferrous* salts; (2) *Ferric oxide*, or *sesquioxide*, Fe_2O_3, from which the *Ferric* salts are derived. The first series of determinations of the vapour density of Ferrous and Ferric chlorides pointed to the formulæ Fe_2Cl_4, and Fe_2Cl_6, and it was supposed that in each of them iron was tetravalent, as shown in the following formulæ:

Ferrous Chloride. Ferric Chloride.

$$\begin{array}{c} Fe=Cl_2 \\ \| \\ Fe=Cl_2 \end{array} \qquad \begin{array}{c} Fe\equiv Cl_3 \\ | \\ Fe\equiv Cl_3. \end{array}$$

Later and more extended researches on the vapour density of these salts have, however, shown that no constant value is obtained until a very high temperature is reached, and that the values then obtained agree approximately with the formulæ $FeCl_2$, and $FeCl_3$. Iron is therefore a *dyad* in the ferrous salts, and a *triad* in the ferric salts.

Ferrous Compounds.

Ferrous Oxide, FeO.—This substance has not been prepared in the pure state, owing to the great readiness with which it absorbs oxygen, passing into the higher oxides. *Ferrous hydroxide*, $Fe(OH)_2$, is thrown down as a white precipitate, when potash or soda is added to a soluble ferrous salt: this white precipitate can only be obtained in complete absence of oxygen, as it at once absorbs this gas, yielding a greenish-brown precipitate of a higher oxide. This oxide colours glass green (see p. 232), and gives the peculiar tint to common bottle-glass. The most important of the ferrous salts are :

Ferrous Sulphate (*Protosulphate of Iron*), $FeSO_4 + 7H_2O$. This soluble salt, sometimes called *green vitriol*, is obtained by dissolving (1) metallic iron, or (2) ferrous sulphide, in sulphuric acid; and is also prepared by the slow oxidation of iron-pyrites, FeS_2:

$$(1)\ Fe + H_2SO_4 = FeSO_4 + H_2;$$
$$(2)\ FeS + H_2SO_4 = FeSO_4 + H_2S.$$

The solution thus obtained yields on evaporation large green crystals of the salt. It is largely used in the manufacture of several black dyes, and is one of the constituents of writing-ink. Like all the ferrous compounds, this salt easily takes up oxygen, producing a new salt called ferric sulphate.

Ferrous chloride, $FeCl_2$.—When dry hydrochloric acid gas is passed over hot metallic iron, ferrous chloride and hydrogen are formed: the hydrated chloride is also produced when iron is dissolved in aqueous hydrochloric acid, green crystals being deposited, having the composition $FeCl_2 + 4\ H_2O$.

Ferrous Carbonate, $FeCO_3$.—This is an insoluble compound, and occurs largely as a mineral called spathose iron ore, which is isomorphous with calc-spar; it also occurs in a less pure form, constituting the *clay-ironstone*, the ore from which a large proportion of our iron is prepared.

Ferrous sulphide, FeS, an invaluable compound formed by fusing equivalent quantities of sulphur and iron together, is employed in the laboratory for the generation of sulphuretted hydrogen (see p. 131). A disulphide, FeS_2, called *iron pyrites*, is found in large quantities in nature, and is much used in the production of sulphuric acid (see p. 124).

Ferric Compounds.

Ferric Oxide, or *Iron Sesquioxide*, Fe_2O_3.—This oxide occurs native as the minerals red hæmatite and specular iron ore, whilst, combined with water, it forms brown hæmatite. It may be readily prepared artificially by heating ferrous sulphate to redness; or by adding a solution of ammonia or caustic potash to a solution of a ferric salt, when the *hydroxide*, $Fe(OH)_3$, falls down as a bulky brownish red powder, which dissolves in acids, forming the ferric salts; when thus acted upon by sulphuric acid, *ferric sulphate*, $Fe_2(SO_4)_3$, is produced; and by hydrochloric acid, *ferric chloride*, $FeCl_3$. Of the ferric salts, the chloride is the most important: the anhydrous salt forms in brilliant black crystals when chlorine gas is passed over heated metallic iron. Solutions of the ferric salts can be reduced by various deoxidizing agents to the corresponding ferrous salts, whilst the latter, in contact with an oxidizing agent, pass into the ferric salts. If for instance, sulphuretted hydrogen gas be led through a solution of ferric chloride, the liquor becomes colourless, ferrous chloride is formed, and a white precipitate of sulphur is thrown down, thus:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

The ferrous- or proto-salts are distinguished by their light green colour, and by their solutions giving (1) a white precipitate with caustic alkalis; (2) a light blue precipitate with potassium ferrocyanide, which rapidly becomes dark: whilst the ferric- or per-salts are yellow-coloured, and their solutions yield (1) a deep-reddish-brown precipitate with the caustic alkalis; and (2) a deep blue precipitate, with potassium ferrocyanide. Ferrous oxide and the ferrous salts are magnetic, whilst the ferric oxide and salts are not magnetic.

The Magnetic, or *Black Oxide*, Fe_3O_4, occurs native, crystallized in octahedra; and, as the mineral *loadstone*. It constitutes one of the most valued ores of iron, and is the oxide formed when iron is oxidized at a high temperature in the air, in oxygen, or in aqueous vapour. The corresponding sulphide, Fe_3S_4. is also magnetic.

Ferric Acid.—The potassium salt of this acid is prepared by fusing ferric oxide and nitre together: the mass yields, with water, a purple-coloured solution, and contains potassium ferrate, K_2FeO_4. It is an exceedingly unstable substance. Neither the acid H_2FeO_4 nor the oxide FeO_3 have been prepared.

Manufacture of Iron.

The oldest method of manufacturing wrought-iron was to reduce it directly from the ore by heating in a wind-furnace with charcoal or coal, and to hammer out the spongy mass of iron thus obtained. This plan can only be economically employed on a small scale and with the purest forms of iron ore, and has been superseded by a more complicated method, applicable, however, to all kinds of iron ore. This consists in the formation of cast-iron as the first product, and the subsequent separation of the carbon and silicon which the cast-iron contains. Cast-iron is manufactured in England chiefly from clay ironstone, which generally occurs in masses, situated in the immediate neighbourhood of a coal seam. The clay ironstone (ferrous carbonate, with clay) is first roasted, in which operation the carbonic acid is driven off, and ferric oxide formed, the ore afterwards being thrown together with coal and limestone, into a blast furnace, the best construction of which is seen in Fig. 67. It has the shape of a double cone (A B, Fig. 67), built of strong firebrick and masonry, and is about fifty feet in height, and fifteen to eighteen feet in width at the broadest part. The furnace is closed at the bottom, the air necessary for the maintenance of the combustion being supplied by a powerful blast, blown through pipes called *tuyeres* (C) ; the mixture of fuel and ore is continually cast in at the top of the furnace (D), as the burning material sinks down, and the molten mass is drawn off at the bottom, so that one furnace often does not stop working for several years. At the lowest part of the structure is the hearth (H), where the melted metal and fused slag collect ; the former is occasionally tapped from the bottom of the hearth, and cast into pigs in moulds made in the sand, whilst the lighter slag, which swims on the surface of the metal, runs continually out from an opening at the upper part of the hearth.

The first chemical change which the roasted iron ore, or impure ferric oxide, undergoes in its passage from the top to the bottom of the furnace, is its reduction to a porous mass of metallic iron, by the carbonic oxide gas proceeding from the lower layers of burning coal. The temperature of this portion of the furnace is, however, much too low to melt the iron ; and it therefore sinks down unchanged, together with the clay and limestone, until it reaches a point at which the heat is greater. Here the second change occurs ; viz., the clay, sand, and other impurities of the ore unite with the limestone to form a fusible silicate of lime called slag, whilst the heated metal, coming in contact with carbon, unites at once with it to form a fusible compound, which runs down to the bottom of the furnace. This in passing through the hottest portion of the furnace, reduces the silica, with which it meets, to silicon, and, combined with this and with the carbon, it forms cast-iron.

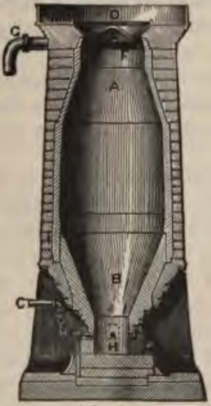


FIG. 67.

The properties and appearance of cast-irons vary much with the quantity of carbon and silicon which they contain ; for cast-iron is not a definite chemical compound of these elements with iron. The carbon is found in cast-iron, (1) as scales of graphite, giving rise to grey and mottled cast-iron ; and (2) in combination, forming white cast-iron. Sometimes sulphur and phosphorus are also found in cast-iron ; but these must be considered as impurities. A great saving of fuel in the working of blast furnaces has lately been effected by employing the heat of combustion of the waste gases—which formerly were allowed to escape and burn at the top of the furnace—

to raise the temperature of the blast of air supplying the furnace. The gases are collected at the top of the furnace by a hood (E), and pass down an iron pipe (G, Fig. 67), which is carried down to the furnaces where the gases are burnt.

Wrought-Iron.—In order to obtain wrought- from cast-iron, the latter must undergo the processes of "refining" and "puddling." These consist essentially in burning out the carbon, silicon, sulphur, and phosphorus, by exposing the heated metal to a current of air in a reverberatory furnace: the melted cast-iron becomes first covered with a coat of oxide, and gradually thickens so much as to allow of its being rolled into large lumps or balls. During this process almost the whole of the carbon escapes as carbonic oxide, and the silicon becomes oxidized to silica, which unites with the oxide of iron and forms a fusible slag; any phosphorus or sulphur contained in the pig-iron is also oxidized in this process. The ball is then hammered to give the metal coherence, and to squeeze out the liquid slag, and the mass afterwards rolled into bars or plates.

Steel.—Another interesting branch of the iron trade is the manufacture of steel. This useful substance is formed when bars of wrought-iron are heated to redness for some time in contact with charcoal: the bar is then found to have become fine-grained instead of fibrous, the substance is more malleable and more easily fusible than the original bar-iron, and is found to contain carbon varying in amount from one to two per cent. Steel possesses several important properties, especially the power of becoming very hard and brittle when quickly cooled, which fits it for the preparation of cutting-tools, &c.: these are, however, generally made of bar-steel which has been previously fused and cast into ingots.

Bessemer Steel.—A most important and very rapid mode of preparing cast-steel, which is both of high scientific interest and industrial value, is that known as the Bessemer process. This process consists in burning out all the carbon and silicon in cast-iron by passing a blast of atmospheric air through the molten metal, and then adding such a quantity of a pure cast-iron to the wrought-iron thus prepared as is necessary to give carbon enough to convert the whole mass into steel: the melted steel is then at once cast into ingots. In this way twenty tons of cast-iron can at one operation be converted into steel in twenty minutes. Bessemer steel is now largely manufactured for railway axles and rails, for boiler-plates, ships, and other purposes, for which it is much more fitted than wrought-iron ; so that this process has revolutionised the old wrought-iron industry.

Ordinary cast iron contains phosphorus, and when this is present in any quantity, it cannot be used for steel making in the ordinary Bessemer converter lined with silica brick, as the phosphorus is not eliminated, and greatly deteriorates the steel. If, however, a so-called basic lining, consisting of lime, be employed in the converter, the whole of the phosphorus finds its way into the slag, and thus a pure steel is obtained.

COBALT.

Symbol Co, *Atomic Weight* 58·6, *Specific Gravity* 8·5.

Cobalt is a reddish-white, very tenacious metal, which is as infusible as iron, and, like the latter metal, is strongly magnetic. It is not found native, but occurs in combination with arsenic and sulphur, as two distinct minerals, *tin white cobalt*, $CoAs_2$, and *cobalt glance*, $CoAsS$. The metal dissolves slowly in sulphuric and hydrochloric acids with evolution of hydrogen. The cobalt compounds are distinguished for the brilliancy of their colour ; they are employed as pigments, and they impart a magnificent blue tint to glass. There are three oxides of cobalt—the monoxide, CoO, the sesquioxide, Co_2O_3, and an oxide, Co_3O_4. The monoxide, on solution in acids, forms the series of well-known and stable *cobaltous* salts, which are pink when hydrated, and blue when anhydrous ; whilst the sesquioxide forms the unstable and little known *cobaltic* compounds. *Cobalt Monoxide*, CoO, is obtained as a brown powder by carefully heating the rose-coloured hydroxide, $Co(OH)_2$, precipitated by potash in solutions of cobalt : and *Cobalt Sesquioxide*, Co_2O_3, is prepared by adding a solution of bleaching-powder to a soluble proto-salt : the oxide Co_3O_4 is obtained by igniting the monoxide in the air.

Cobalt Chloride, $CoCl_2$, is a soluble salt obtained by acting on the oxide or on the metallic ore with hydrochloric acid ;

the solution yields on evaporation pink crystals of the hydrated chloride, or if further heated blue crystals of the anhydrous salt.

The *Nitrate*, $Co(NO_3)_2$, and *Sulphate*, $CoSO_4$, are also soluble salts; the latter is isomorphous with magnesium sulphate. *Cobalt Sulphide*, CoS, is a black powder, insoluble in dilute acids.

Cobalt compounds can be easily recognised by the deep blue tint which very minute traces impart to glass, or to a borax bead, made by fusing borax into a colourless mass on the loop of a platinum wire.

NICKEL.

Symbol Ni, *Atomic Weight* 58·6, *Specific Gravity* 8·8.

Nickel occurs in large quantities, combined with arsenic, as *kupfernickel*, NiAs; also together with cobalt in *speiss;* and it is now prepared in considerable quantities for the manufacture of German silver, (an alloy of nickel, zinc, and copper,) and is also largely employed for plating articles of brass and steel. Nickel is a white, malleable, and tenacious metal; it melts at a somewhat lower temperature than iron, and is strongly magnetic, but loses this property when heated to 350°. There are two oxides of nickel, the *monoxide*, NiO, and the *sesquioxide*, Ni_2O_3: the former of these gives rise to the nickel salts, which possess a peculiar apple-green colour. The monoxide is obtained by heating the nitrate or carbonate, or by precipitating a soluble nickel salt with caustic potash, and heating the apple-green hydroxide, $Ni(OH)_2$, which is thrown down. The sesquioxide is a black-powder, prepared by adding a solution of bleaching-powder to a soluble nickel salt.

The important soluble nickel salts are the *sulphate*, $NiSO_4 + 7H_2O$, crystallizing in green prisms; the *nitrate*, $Ni(NO_3)_2$; and the *chloride*, $NiCl_2$. Like cobalt, nickel forms a black sulphide, NiS, insoluble in dilute acids. The nickel salts may be distinguished from those of the former metal by imparting a reddish-yellow colour to the borax bead, as well as by their green colour.

When pure dry carbon monoxide is passed over finely divided nickel at 30°, a peculiar volatile liquid having the composition $Ni(CO)_4$ and termed *nickel carbon monoxide* is obtained. It solidifies at − 25°, boils at 43°, and has a sp. gr. of 1·3185 at 17°; its vapour on heating at 60° explodes violently, and if passed through a heated tube mixed with other gases deposits a mirror of pure nickel. This remarkable compound is the only one of the kind yet isolated, but it appears that iron does form a similar compound, which has however not yet been prepared in a pure condition. It is proposed to employ the above reaction for preparing pure metallic nickel.

LESSON XXV

CLASS IX.—THE CHROMIUM GROUP

Chromium, Molybdenum, Uranium, Tungsten.

CHROMIUM

Symbol Cr, *Atomic Weight* 52·1, *Specific Gravity* 7·3

Chromium is a substance whose compounds do not occur very widely distributed, or in large quantities: but they are nevertheless, much employed in the arts as pigments, many of them possessing a fine bright colour (whence its name χρῶμα, colour). The chief ore of this metal is chrome ironstone, $FeOCr_2O_3$, a compound isomorphous with magnetic oxide of iron, found in America, Sweden, and the Shetlands; a crystalline lead chromate, $PbCrO_4$, also occurs in some quantity. Pure chromium appears to be the most infusible of all the metals, as it cannot be melted at a temperature sufficient to fuse and volatilize platinum: it has, however, been obtained by another process, in the form of bright crystals belonging to the cubic system. Chromium unites with oxygen in four different proportions to form:

(1) Chromium Monoxide, CrO.
(2) Chromium Sesquioxide, Cr_2O_3.
(3) Chromo-Chromic Oxide, $CrO.Cr_2O_3$.
(4) Chromium Trioxide, CrO_3.

The first two of these oxides are basic and yield corresponding chlorides and salts termed respectively the *chromous* and the *chromic* salts, thus CrO, $CrCl_2$; Cr_2O_3, $CrCl_3$: the third oxide is a neutral body, corresponding to the magnetic oxide of iron: and the fourth oxide forms an acid with water.

Chromous Compounds.

Chromium Monoxide, CrO, is only known in the hydrated state, as both it and its compounds absorb oxygen with great avidity. The hydroxide, $Cr(OH)_2$, is prepared as a brown precipitate by adding potash to the solution of chromium dichloride.

Chromium Dichloride, $CrCl_2$, is a white crystalline body, which dissolves in water, forming a blue solution. It is obtained by passing hydrogen over heated chromic chloride.

Chromic Compounds.

Chromium Sesquioxide, or *Chromic Oxide*, Cr_2O_3, is a dark green, perfectly stable powder, obtained by igniting the hydroxide, $Cr(OH)_3$, formed by precipitating any soluble chromic salt with ammonia. It is employed as a green colour for painting on porcelain, and gives rise to the green of the emerald. A splendid green colour is also obtained by heating potassium bichromate with boron trioxide: on dissolving in water, a grass-green hydroxide remains behind, which is termed Guignet's green,

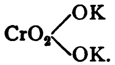
$$Cr_4H_6O_9 = Cr_2O_3 + 2Cr(OH)_3.$$

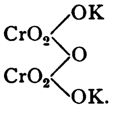
Chromic Chloride, $CrCl_3$.—The anhydrous chloride is obtained as a sublimate, in beautiful violet crystals, by passing a current of chlorine gas over a red-hot mixture of chromium sesquioxide and charcoal. These crystals do not dissolve easily in water, but are readily soluble if a trace of chromium dichloride is present. The most ready way of preparing a solution of chromic chloride is to boil a solution of chromic acid or of a chromate with hydrochloric acid and alcohol, the red or yellow solution after a few minutes being changed to a deep greenish-blue colour. A solution of chromic sulphate

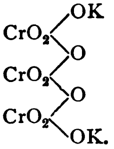
$Cr_2(SO_4)_3$, may be obtained in the same way, by substituting sulphuric acid for hydrochloric acid. Chromium sulphate forms a series of *alums* with potassium and ammonium sulphates, which have a deep purple tint, and are isomorphous with common alum, $Cr_2(SO_4)_3 + K_2SO_4 + 24\ H_2O$. The chromic salts are green, but violet-coloured modifications also occur.

Chromic Acid and Chromates.

If any chromic compound be fused with potassium carbonate, it becomes oxidized, and a soluble yellow chromate is formed, K_2CrO_4 : this is the mode in which the chromium compounds are prepared from chrome-iron ore. This yellow chromate is isomorphous with potassium sulphate and manganate. When sulphuric acid is added to a solution of the yellow salt in sufficient quantity to combine with half the base, large red crystals of the *anhydrochromate*, $K_2Cr_2O_7$, separate out. This salt is commonly called bichromate of potash, and is largely used for the preparation of the chrome pigments. If to the solution of the bichromate a solution of chromium trioxide be added, a third salt, termed *potassium trichromate*, $K_2Cr_3O_{10}$, crystallizes out. The constitution of these three salts may be represented as follows :

(1)


(2)


(3)


If lead chromate is heated with a solution of a caustic alkali an orange-red basic chromate is formed having the composition $CrO_2 \left\{ \begin{matrix} OPb \\ OPb \end{matrix} \right\} O$.

Chromium trioxide, CrO_3, is obtained in the form of long ruby-red needle-shaped crystals by adding an excess of strong sulphuric acid to a concentrated solution of the bichromate. The crystals are very soluble in water, forming an acid solution of chromic acid, H_2CrO_4. The excess of sulphuric acid may be removed by washing with concentrated nitric acid, and the crystals then dried in a glass tube in a current of air. The crystals of chromium trioxide are very easily reduced to sesquioxide in presence of organic matter; so energetic is this evolution of oxygen, that ignition occurs when alcohol is dropped on the dry crystals.

If a solution of chromium trioxide or of potassium bichromate be heated with hydrochloric acid, chromic chloride is formed and chlorine liberated; whereas, if chromium trioxide be heated with sulphuric acid, a chromic sulphate is formed and oxygen gas is given off.

$$(1)\ 2CrO_3 + 12HCl = Cr_2Cl_6 6H_2O + 3Cl_2.$$
$$(2)\ 2CrO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + O_3 + 3H_2O.$$

The chief of the insoluble chromates are *lead chromate*, $PbCrO_4$, or *chrome yellow*, obtained by precipitating potassium chromate by a soluble lead salt, and largely used as a pigment and for other purposes in the arts; *silver chromate*, Ag_2CrO_4, a characteristic, deep-red coloured precipitate; and *barium chromate*, $BaCrO_4$, also a yellow insoluble powder.

Chromium Oxychloride, or *Chromyl Chloride*, $CrO_2\left\{\begin{matrix}Cl\\ Cl.\end{matrix}\right.$—A compound resembling sulphuryl chloride in constitution is obtained by distilling potassium bichromate, sulphuric acid and common salt. It is a dark red, strongly fuming liquid; it boils at 181°, has a specific gravity of 1·92; and the density of its vapour is 77·7 (H = I). If potassium bichromate be dissolved in warm hydrochloric acid, large red crystals separate out on cooling: these consist of potassium chloro-chromate, $KClCrO_3$, a substance intermediate between chromium oxychloride and potassium chromate. We have thus:

Chromium Oxychloride.	Potassium Chloro-chromate.	Potassium Chromate.
$CrO_2\left\{\begin{matrix}Cl\\ Cl.\end{matrix}\right.$	$CrO_2\left\{\begin{matrix}OK\\ Cl.\end{matrix}\right.$	$CrO_2\left\{\begin{matrix}OK\\ OK.\end{matrix}\right.$

The presence of chromium and its compounds can be easily detected by the formation of soluble yellow-coloured salts with the alkali-metals, yielding insoluble lead and silver compounds, and capable of easy reduction to green solutions in presence of organic matter. Chromium sesquioxide imparts to glass or borax a fine deep green colour.

It may also be detected by the splendid, but very fugitive, blue coloration which is produced when hydrogen dioxide is added to a very dilute solution of chromic acid: this blue colour is due to the formation of a still higher oxide of chromium, analogous to permanganic acid, and termed perchromic acid, which, however, very readily decomposes.

MOLYBDENUM

Symbol Mo, *Atomic Weight* 95·8.

The chief ore of this metal is *molybdenum disulphide*, MoS_2, a mineral in appearance resembling graphite. The metal possesses a silver-white lustre, is brittle and melts at an extremely high temperature, oxidizing on heating in the air to *molybdenum trioxide*, MoO_3, a yellow powder which acts as an acid, forming with bases salts called *molybdates*. The compounds of molybdenum do not occur frequently, and are not used in the arts. Molybdic acid is, however, used as a reagent in the laboratory for detecting small quantities of phosphoric acid (see p. 149).

TUNGSTEN.

Symbol W (*Wolfram*), *Atomic Weight* 184.

This metal occurs in tolerably large quantities combined with ferrous oxide in the mineral *wolfram*, $FeWO_4$, and also with lime as *scheelite*, $CaWO_4$. The fused metal is white and brittle, possessing a specific gravity of 19·1. Tungsten is employed occasionally in the arts: the addition of a small quantity imparts a great degree of hardness and other valuable qualities to steel. Three oxides of tungsten are known, —*Tungsten dioxide*, WO_2; *Tungsten trioxide*, WO_3; and W_2O_5 which may be regarded as a compound of WO_2 and WO_3. The dioxide is obtained as a brown powder by heating the trioxide in an atmosphere of hydrogen; the trioxide, which is sometimes called tungstic acid, is obtained as an insoluble yellow powder by heating the native calcium tungstate with nitric acid. Tungsten trioxide forms a variety of somewhat complicated salts. The sodium compound is soluble, and has been used to add to the starch employed to stiffen light fabrics, the tungstate rendering the fabric uninflammable.

URANIUM.

Symbol U, *Atomic Weight* 239, *Specific Gravity* 18·4.

Uranium is a metal which occurs but sparingly in nature, existing combined in two somewhat rare minerals, *pitchblende*, U_3O_8, or $UO_2 + 2\,UO_3$, and *uranite*. The metal is of a steel-white colour and does not oxidize in dry air at ordinary temperatures, but when strongly heated it burns brilliantly. There are two oxides which form salts, viz., *uranous oxide*, UO_2, and *uranic oxide*, UO_3: the uranous salts are green, whilst the uranic compounds are yellow; and these latter solutions give yellow precipitates with an alkali, in which the uranic oxide acts as an acid, forming a uranate of the base; thus with potash we obtain $K_2U_2O_7$. The sulphide is insoluble and of a yellowish-brown colour. The chief application of uranium compounds is for the purpose of glass-staining; the uranous oxide imparts a fine black, and the uranic oxide a beautiful yellow, to glass: uranium compounds are also now used in photography.

CLASS X.—THE TIN GROUP.

Tin, Titanium, Zirconium, Germanium.

TIN.

Symbol Sn (*Stannum*), *Atomic Weight* 117·8,
Specific Gravity 7·3.

The ores of tin—although this metal has been known from very early times—occur in but few localities, and the metallic tin is not found in nature. The chief European sources of tin are the Cornish mines, where it is found as tin dioxide or tinstone, SnO_2. It is in all probability from these mines that the Phœnicians and Romans obtained all the tin which they employed in the manufacture of bronze. Tinstone is also met with in Australia in Malacca, in Borneo, and Mexico. In order to prepare the metal, the tinstone is crushed and washed, to remove mechanically the lighter portions of rock with which it is mixed, and the purified ore then placed in a reverberatory furnace with anthracite or charcoal and a small quantity of lime: the oxide is thus reduced, and the liquid metal, together with the slag, consisting of silicate of lime, falls to the lower part of the furnace. The blocks of tin, still impure, are then refined by gradually melting out the pure tin, leaving an impure alloy behind. English tin generally contains traces of arsenic, copper, and other metals; that imported from Banca is nearly chemically pure.

Tin possesses a white colour resembling that of silver; it is soft, malleable, and ductile, but possesses little tenacity, a wire two mms, in diameter breaking with a weight of sixteen kilos. When bent, pure tin emits a peculiar crackling sound. Tin melts at 235°, and is not sensibly volatile. It does not lose its lustre on exposure to the air, whether dry or moist, at the ordinary temperature, but if strongly heated it takes fire, forming a white powder of stannic oxide (sometimes termed putty powder). Hydrochloric acid dissolves tin with the evolution of hydrogen and the formation of stannous chloride: nitric acid also attacks the metal with great energy, nitrous fumes being given off and stannic oxide being left as a white powder. There are two well-marked oxides of tin.

Tin Monoxide, or *Stannous Oxide*, SnO.—This is a black powder prepared by heating stannous hydroxide, $Sn_2O(OH)_2$, in an atmosphere of carbonic acid; it rapidly absorbs oxygen from the air passing into stannic oxide. The hydroxide falls as a white powder when a solution of stannous salt is added to an alkaline carbonate.

Tin Dioxide, or *Stannic Oxide*, SnO_2, occurs native as tinstone; and it can be prepared as a hydrate in two conditions, possessing totally different properties. If tin be oxidized by nitric acid, hydrated stannic oxide, H_2SnO_3, is produced as a white powder, insoluble in acids; if, on the other hand, an alkali be added to a solution of stannic chloride a white precipitate of hydrated stannic oxide is formed, which is readily soluble in acids. Both of these varieties of hydrated stannic oxide form salts, the insoluble compound having been termed *metastannic*, and the soluble compound *stannic* acid. Sodium stannate, $Na_2SnO_3+4H_2O$, formed by boiling stannic oxide with soda, is largely used in calico-printing as a "mordant," and then termed "tin prepared liquor."

Tin Dichloride, or *Stannous Chloride*, $SnCl_2$, is obtained by dissolving tin in hydrochloric acid, and separates out in needle-shaped crystals, $SnCl_2 + 2\ H_2O$, when the solution is concentrated. Stannous chloride is termed "tin salts," in commerce; it is largely manufactured for the calico-printer and dyer, who use it as a mordant.

Tin Tetrachloride, or *Stannic Chloride*, $SnCl_4$. is obtained by passing chlorine gas over metallic tin; it is a colourless liquid, boiling at 120° C. and having a vapour density of 9·2. It fumes strongly in the air, and forms a crystalline hydrate when a small quantity of water is added, which easily dissolves in an excess. Stannic chloride is also used by dyers, and is prepared for this purpose by dissolving tin in cold nitro-hydrochloric acid.

Of the sulphides of tin, *Stannous Sulphide*, SnS, and *Stannic Sulphide*, SnS_2, are the most important: the former is blackish-grey, and the latter a bright yellow crystalline powder, known as mosaic gold, soluble in alkaline sulphides.

Tin can easily be distinguished in solution by the formation of a splendid purple colour called *purple of Cassius*, obtained when gold chloride, $AuCl_3$, is added to a dilute solution of stannous chloride. Tin is also easily reduced before the blowpipe in the form of white malleable beads, which are soluble in hydrochloric acid. The solution thus obtained produces with a solution of mercuric chloride a white precipitate of calomel, which on heating becomes black owing to formation of metallic mercury.

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4.$$
$$2HgCl + SnCl_2 = Hg_2 + SnCl_4.$$

Tin withstands the oxidizing action of the air, and is therefore largely used in the arts for covering and thus protecting iron plates, or for "tin-plating," and also for preparing several valuable alloys, as pewter, Britannia metal, plumbers' solder, bronze, bell-metal, &c.

TITANIUM.

Symbol Ti, *Atomic Weight* 48.

Titanium is a rare metal, only known in the form of a grey powder, and resembling tin in its chemical properties. It is found in combination with oxygen in the mineral *rutile*, TiO_2. The oxides of titanium correspond to those of tin; viz. *titanous* and *titanic* oxides, TiO and TiO_2. Titanium and its compounds are not used in the arts, but a compound of this metal is met with in blast furnaces, crystallizing in red cubes, which for some time was supposed to be metallic titanium, but since has been shown to possess the formula $Ti(CN)_2 + 3Ti_3N_2$. Titanium is distinguished by its power of uniting directly with nitrogen at high temperatures.

Tin and *Titanium* are tetravalent elements, and form with *Silicon* a natural group, to which the rare metals ZIRCONIUM ($Zr=90$) and THORIUM ($Th = 231{\cdot}5$) are added. The first of these occurs in the mineral *zircon*, SiO_2ZrO_2, and, like silicon, has been obtained in several allotropic modifications; whilst the latter is found in *thorite*, a very rare mineral.

Germanium ($Ge=72{\cdot}75$) the most recently discovered metal of this group, is contained in certain specimens of a silver ore known as Argyrodite. Its most characteristic compound is the sulphide GeS_2, which is a white substance insoluble in water. Germanium is identical with Mendelejeff's *Ekasilicon* (see p. 266).

LESSON XXVI

CLASS XI.—THE ANTIMONY GROUP

Antimony, Bismuth, Vanadium

ANTIMONY

Symbol Sb (*Stibium*), *Atomic Weight* 120, *Specific Gravity* 6·71

Metallic antimony occurs native, but its chief ore is the trisulphide, Sb_2S_3. The metal is easily reduced by heating the sulphide with about half its weight of metallic iron, when ferrous sulphide and metallic antimony are formed:

$$Sb_2S_3 + 3Fe = Sb_2 + 3FeS.$$

Antimony may also be reduced by mixing the ore with coal and heating in a reverberatory furnace. Antimony is a bright bluish-white coloured metal crystallizing in rhombohedra, isomorphous with arsenic. It is very brittle, and can be powdered in a mortar; it melts at 450°, and may be distilled at a white heat in an atmosphere of hydrogen. Antimony undergoes no alteration in the air at ordinary temperatures, but rapidly oxidizes if exposed to air when melted, and, if heated more strongly, takes fire and burns with a white flame, giving off dense white fumes of antimony trioxide. Antimony is not affected either by dilute hydrochloric or sulphuric acids: nitric acid attacks the metal, converting it into white insoluble antimony pentoxide. Nitro-hydrochloric acid dissolves antimony easily. The alloys of antimony are largely used in the arts. Of these type-metal (an alloy of lead and antimony) is the most important: it contains 17 to 20 per cent. of the latter metal.

The two important oxides of antimony, (1) *antimony trioxide*, Sb_2O_3, (2) *antimony pentoxide*, Sb_2O_5 (sometimes called antimonic acid), correspond to those of arsenic (see p. 154). A third oxide exists unknown in the arsenic series; this is an intermediate *tetroxide* having the composition Sb_2O_4.

Antimony Trioxide, Sb_2O_3.—This oxide gives rise to the important series of salts of antimony used in medicine ; it is obtained in crystalline needles, which are isomorphous with the rare form of arsenic trioxide (see p. 154). Antimony trioxide has also been observed to crystallize in octahedra : hence these two oxides are said to be *iso-dimorphous*. The best mode of preparing the pure oxide is by decomposing antimony trichloride with an alkaline carbonate, when the oxide is precipitated as a white powder :

$$2SbCl_3 + 3Na_2CO_3 = Sb_2O_3 + 6NaCl + 3CO_2.$$

Antimony trioxide dissolves, when boiled with a solution of cream of tartar (hydrogen potassium tartrate), and on concentration the solution deposits crystals of tartar emetic (see also "Tartaric Acid") : antimony trioxide also dissolves in hydrochloric acid, yielding a solution of the trichloride, which is rendered turbid by the addition of water owing to the formation of an insoluble *antimony oxychloride* SbOCl :

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

Antimony Pentoxide, Sb_2O_5, is obtained by acting on antimony with strong nitric acid, or by decomposing the pentachloride of antimony with water, and gently heating the precipitated hydrate. It is a light straw-coloured powder, which loses oxygen at a red heat, and is converted into the intermediate oxide $Sb_2O_3Sb_2O_5$. Antimony pentoxide forms salts with the alkalis called *antimoniates*, corresponding to the arsenates, from which antimonic acid, $HSbO_3$, can be separated as a white powder. The hydrate obtained by acting with water on the pentachloride is termed *metantimonic acid*, $H_4Sb_2O_7$. The acid metantimoniates easily decompose into the ordinary antimoniates. The acid sodium metantimoniate, $Na_2H_2Sb_2O_7 + 6\ H_2O$, is distinguished as being the only insoluble sodium salt known. It is precipitated by adding a solution of potassium metantimoniate to a sodium salt.

The intermediate *tetroxide*, Sb_2O_4, is obtained by heating the metal or the pentoxide in the air until no further change occurs

Finely-powdered metallic antimony takes fire spontaneously when thrown into chlorine gas, with formation of the two chlorides of antimony.

Antimony Trichloride, $SbCl_3$, is obtained as a buttery mass by passing chlorine gas over an excess of metallic antimony, or by dissolving the metal or sulphide in hydrochloric acid to which a little nitric acid has been added : on distilling the liquid thus obtained the trichloride volatilizes, and, on cooling, solidifies to a mass of white crystals. These melt at 72°, and the liquid boils at 180°. When a solution of the trichloride in hydrochloric acid is poured into water, a white precipitate of *powder of algaroth* is formed, possessing the composition $2\ SbOCl + Sb_2O_3$. Antimony oxychloride, SbOCl, is formed when the trichloride is heated with alcohol to a temperature of 160°.

Antimony Pentachloride, $SbCl_5$, is a mobile strongly-fuming liquid, obtained by passing an excess of chlorine over the trichloride or the metal. On distillation it decomposes into the trichloride and free chlorine.

The *Sulphides of Antimony*, Sb_2S_3 and Sb_2S_5, correspond to the oxides, and are capable of uniting with the alkaline sulphides to form a class of soluble salts. Thus sodium sulphantimoniate is $Na_3SbS_4 + 9\ H_2O$.

Antimony Hydride (or *Stibine*) SbH_3.—Like arsenic, antimony unites with hydrogen to form a gaseous compound, SbH_3, analogous to AsH_3, *arseniuretted hydrogen*. The gas is evolved, together with hydrogen, when an antimony salt is brought in contact with zinc and dilute acid. Like the corresponding arsenic compound, it burns with a bluish flame, evolving white-coloured antimony trioxide, and is decomposed at a red-heat with deposition of metallic antimony.

The detection and separation of arsenic and antimony is a subject of much importance in medical jurisprudence, as both substances exhibit poisonous characters, and closely resemble one another in their reactions : still, with care, it is easy to discriminate between these two metals, and to detect with certainty a very minute quantity of either when present in the body of an animal.

BISMUTH.

Symbol Bi, *Atomic Weight* 208·4 *Specific Gravity* 9·8.

This metal is found in small quantities in the native state, but occurs more frequently as a sulphide Bi_2S_3; it is easily reduced to the metallic state, and then exhibits a pinkish-white colour. It crystallizes in large rhombohedra, which can scarcely be distinguished from cubes; it melts at 264°, and is volatilized at a white-heat. Bismuth does not oxidize in dry air at the ordinary temperature, but if heated strongly it burns with a blue flame, forming an oxide; it also takes fire when thrown into chlorine gas, forming $BiCl_3$. Bismuth dissolves easily in nitric acid. The metal is chiefly used as an ingredient of fusible metal; its compounds are also used in medicine and as pigments. Two oxides of bismuth are known, *Bismuth trioxide*, Bi_2O_3, and *Bismuth pentoxide*, Bi_2O_5. The first of these is a pale yellow powder, formed when the metal is roasted in the air; the second oxide is obtained by dissolving the first in potash, and precipitating the pentoxide by nitric acid and heating: it is a reddish-brown powder. Like the corresponding antimony compound, bismuth pentoxide forms with the alkalis soluble salts.

Bismuth nitrate, $Bi(NO_3)_3 + 5H_2O$, is the most important soluble salt of bismuth; the *sulphide*, Bi_2S_3, is a black insoluble compound; the *trichloride*, $BiCl_3$, is obtained by heating the metal in chlorine.

One of the most striking peculiarities of the bismuth compounds is, that solutions of the salts become milky on the addition of water, owing to the formation of insoluble basic compounds. Thus $Bi(OH)_2NO_3$ is formed as a white powder, used in medicine, by adding water to a solution of the normal nitrate; and an oxychloride, $BiOCl$, is precipitated by adding water to the trichloride. Metallic bismuth is easily reduced from its compounds before the blowpipe, as a brittle bead.

VANADIUM.

Symbol V. *Atomic Weight* 51·2.

This is a very rare metal: its compounds occur in small quantity in certain iron ores, and also in combination as lead vanadate. It forms an interesting oxide, termed *Vanadium pentoxide*, V_2O_5, which yields salts called *vanadates* isomorphous with arsenates and phosphates, and also forms an oxychloride, $VOCl_3$, corresponding to phosphorus oxychloride, $POCl_3$.

Tantalum, Ta, *Atomic Weight* 182; and **Niobium**, Nb, *Atomic Weight* 94, are two very rare metals occurring, generally together, in a few rare minerals such as *columbite* and *tantalite*. They form pentoxides, Ta_2O_5 and Nb_2O_5, and pentachlorides, $TaCl_5$ and $NbCl_5$.

CLASS XII.—THE GOLD AND PLATINUM GROUP.

Gold, Platinum, and the rare Platinum-like Metals.

GOLD.

Symbol Au (*Aurum*), *Atomic Weight* 196·7,
Specific Gravity 19·3.

Gold is always found in the metallic state: it occurs in veins in the older sedimentary or in the plutonic rocks, and in the detritus of such rocks; it occurs in traces in the sand of most rivers, and although found generally in small quantities, it is a widely diffused metal. Previous to the discoveries of the gold-fields of California and Australia, it was obtained from certain iron pyrites. In order to obtain the gold, the detritus or sand which contains the metal is washed in a "cradle" or other arrangement, by means of which the lighter particles of mud or mineral are washed away, whilst the heavier grains of gold sink to the bottom of the vessel. When gold has to be workèd in the solid rock, the mineral is crushed to powder and then shaken up with mercury, and the gold thus extracted by amalgamation.

Gold possesses a brilliant yellow colour, and, in thin films, transmits green light; it is nearly as soft as lead and can be drawn out into fine wire, being the most malleable of all the metals. It does not tarnish at any temperature, in dry or moist air, nor is it, like silver, affected by sulphur; it is not acted upon by any single acid (except selenic), but dissolves in presence of free chlorine and in nitro-hydrochloric acid. At high temperatures gold is slightly volatile. Pure gold is best prepared by dissolving the ordinary metal in aqua regia, and adding ferrous sulphate, which is oxidized to ferric salt and precipitates the gold as a brown powder. The *standard gold* of our country is an alloy of gold and copper in the proportion of 11 of gold to 1 of copper, or 8·33 per cent. of the latter metal : this alloy is harder and more fusible, but less ductile, than pure gold.

Gold unites with oxygen in two proportions, forming *Gold suboxide*, Au_2O, and *Gold trioxide*, Au_2O_3. Neither of these oxides form salts with acids ; but the latter unites with bases to form compounds called *aurates:* thus *potassium aurate* is $KAuO_2$. Gold trioxide is obtained by adding zinc oxide or magnesia to a solution of gold trichloride; the oxide falls as a brown powder, from which the zinc can be separated by nitric acid. Gold trioxide decomposes, in direct sunlight, into metal and oxygen, and is also reduced when heated to a temperature of about 250°. The most important compound of gold trioxide is fulminating gold. This substance is obtained by acting on a solution of gold with excess of ammonia ; a yellow-brown powder is precipitated, which, when dry, explodes very easily when heated to 100°, or when struck with a hammer. There are two gold chlorides known : (1) *Gold monochloride*, AuCl, obtained as an insoluble white mass when gold trichloride is heated to the melting-point of tin ; (2) *Gold trichloride*, $AuCl_3$, obtained when gold is dissolved in aqua regia. This is the most important compound of gold. On evaporating the solution, crystals of a compound of gold trichloride and hydrochloric acid are deposited. Gold trichloride also forms crystalline compounds with the alkaline chlorides.

Gold salts can be easily recognized by the brown precipitate of metallic gold formed on addition of ferrous salts, which can be reduced to a globule before the blowpipe :

$$2AuCl_3 + 6FeSO_4 = 2Au + 2Fe_2(SO_4)_3 + 2FeCl_3;$$

and also by the formation of a purple colour (purple of cassius), when gold trichloride is added to a dilute solution of a mixture of the two tin chlorides (p. 254).

PLATINUM.

Symbol Pt, *Atomic Weight* 194·5, *Specific Gravity* 21·5.

Platinum is a comparatively rare metal, which always occurs in the native state, and generally alloyed with five other metals, viz. palladium, rhodium, iridium, osmium, and ruthenium. This alloy occurs in small grains in detritus and gravel in Siberia and Brazil; it has not been found *in situ* in the original rock, which probably belongs to the old plutonic series.

The original mode of obtaining the metal was to dissolve the ore in aqua regia, and precipitate the platinum (together with several of the accompanying metals) with sal-ammoniac, as the insoluble double chloride of ammonium and platinum, $2NH_4Cl+PtCl_4$. This precipitate, on heating, yields metallic platinum in a finely divided or spongy state; this sponge, if forcibly pressed and hammered when hot gradually assumes a coherent metallic condition, the particles of platinum welding together, when hot, like iron. An improved mode of preparing the metal has been proposed by Deville, the ore being melted in a very powerful furnace heated with the oxy-hydrogen blowpipe. In this way a pure alloy of platinum, iridium, and rhodium is formed, the other constituents and impurities of the ore either being volatilized by the intense heat, or absorbed by the lime of which the crucible is composed. This alloy is in many respects more useful than pure platinum, being harder and less easily attacked by acids than the pure metal.

Platinum possesses a bright white colour, and does not tarnish under any circumstances in the air; it is extremely infusible, and can only be melted by the heat of the oxy-hydrogen blowpipe. It is unacted upon by the ordinary acids, on which account platinum vessels are much used in the laboratory; it is, however, dissolved by aqua regia, and attacked by caustic alkalis at high temperatures. When finely divided, metallic platinum has the power of condensing gases on to its surface in a remarkable degree: the effect of bringing spongy platinum in contact with a mixture of oxygen and hydrogen has already been mentioned.

Platinum and oxygen unite in two proportions to form—(1) *Platinum monoxide*, PtO; and (2) *Platinum dioxide*, PtO_2 The first of these oxides is a black powder, easily decomposed on heating, and yielding a series of unstable salts; the second is obtained as a brown hydrate, by adding to a solution of platinic nitrate half its equivalent of caustic potash: the hydrate, when heated, first loses its water, forming the anhydrous oxide, and then parts with its oxygen, leaving the metal. *Platinum dichloride*, $PtCl_2$, is a green insoluble powder, obtained by heating the higher chloride to 200°. *Platinum tetrachloride*, $PtCl_4$, is the most important platinum compound. It is obtained as a yellowish-red solution by dissolving the metal in aqua regia; on evaporation, crystals of a compound of platinum tetrachloride with hydrochloric acid separate out. Platinum tetrachloride combines with many alkaline chlorides to form double salts: these compounds with potassium, rubidium, cæsium, and ammonium are very slightly soluble in water, and are isomorphous, crystallizing in cubes; whilst the sodium salt is soluble, and crystallizes in large prisms.

Platinum dichloride, when acted upon by ammonia, gives rise to several very remarkable compounds, containing platinum, nitrogen, and hydrogen: these substances act as bases, and form a well-defined series of salts. These salts may be considered as molecules of ammonium, in which the hydrogen has been partly replaced by either diatomic or tetratomic platinum.

[For the properties of the rare metals, palladium, rhodium, ruthenium, iridium, and osmium, the larger manuals must be consulted.]

THE NATURAL ARRANGEMENT OF THE ELEMENTS.

The table shown on page 264 contains all the elements whose atomic weights are well ascertained, arranged according to those weights, beginning with the lowest, namely hydrogen. An examination of the table shows that a remarkable relationship exists between the atomic weight and the properties of the element. Thus if we take the elements from lithium to chlorine we find they fall into the two following groups:

Li 7	Be 9	B 11	C 12	N 14	O 16	F 19.
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·5.

Here we see that by simply writing them in this order we get the analogous elements coming under one another. Suppose again we take the following seven elements which begin with potassium, we find exactly the same taking place.

K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55.

TABLE SHOWING THE GROUPING OF THE ELEMENTS, OR THE PERIODIC SYSTEM OF THE ELEMENTS (*Mendeléeff*).

Groups.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series.	— R_2O	— R_2O_2 or RO.	— R_2O_3 —	RH_4 R_2O_4 or RO_2	RH_3 R_2O_5	RH_2 R_2O_6 or RO_3	RH R_2O_7	(R_2H) Hydrogen Compounds. R_2O_8 or RO_4 } Higher Oxygen Compounds.
1	1 H							
2	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35·5 Cl	
4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56. Co 59. Ni 59.
5	63 Cu	65 Zn	69 Ga	73 Ge	75 As	78 Se	80 Br	
6	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—	Ru 104. Rh 104. Pd 106.
7	108 Ag	112 Cd	114 In	118 Sn	120 Sb	125 Te	127 I	
8	Cs 133	Ba 137	La 138	Ce 140	Di 142	—	—	— — —
9	—	—	—	—	—	—	—	
10	—	—	Yb 173	—	Ta 182	W 184	—	Os 191. Ir 193. Pt 195.
11	197 Au	200 Hg	204 Tl	207 Pb	208 Bi	—	—	
12	—			Th 234	—	U 239	—	

We can thus arrange the whole of the elements in groups of seven, as shown in the table, except that in three cases we have three elements with atomic weights nearly alike forming an eighth division of a group. In the vertical series we find the various groups of naturally allied elements, such as the alkali-metals, carbon group, nitrogen group, &c., whilst in the horizontal series the properties change regularly from one group to another. This is seen not only in the chemical properties, such as their power of combination with the maximum number of atoms of oxygen or hydrogen, but also in many of their physical properties. Thus the specific gravity of the series beginning with silver is as follows:

	Ag	Cd	In	Sn	Sb	Te	I
Sp. Gr. =	10·5	8·65	7·42	7·29	6·7	6·25	4·95.

It appears, therefore, that matter becomes endowed with similar properties when the atomic weight has increased by 16, 33, or 50 units, or in other words *the properties of the elements are periodic functions of the atomic weights.* This was first enunciated by Newlands, and afterwards more thoroughly worked out by the Russian chemist Mendeléeff, and by Lothar Meyer, and is known as *the periodic law.*

Further examination of the table shows that other relationships exist between many of the elements: thus it frequently happens that the elements of one vertical group are connected by isomorphism or by analogous chemical properties with those in a neighbouring horizontal series. Thus vanadium, showing its close connection with phosphorus by its volatile oxychloride and by the isomorphism of the vanadates with the phosphates, is allied in its chemical characters with niobium and also with chromium and molybdenum.

These last two elements are connected with sulphur by the isomorphism of the chromates, molybdates, and sulphates, just as manganese and chlorine are connected by the isomorphism of the permanganates and the perchlorates. Silver, on the one hand, exhibits analogies with copper and mercury, but, on the other, the isomorphous relations which it exhibits to sodium place it near the metals of the alkalis.

Prediction of New Elements. In the above table a number of gaps will be noticed where there is no element known

with the atomic weight required. When Mendeléeff first brought out this table, a gap existed between Ca 40 and Ti 48, and a double gap between Zn 65 and As 75. He predicted that elements would yet be discovered to fill these three gaps, and from the position these occupied with regard to the other elements he foretold the properties which such elements would possess, naming them Ekaboron, Ekaluminium, and Ekasilicon. These three elements have since been discovered, and are now known as Scandium, Gallium, and Germanium; it has been found that they possess properties which fulfil Mendeléeff's predictions in a most remarkable manner.

LESSON XXVII

SPECTRUM ANALYSIS

AN entirely new branch of chemical analysis, of great delicacy, simplicity, and importance, has been developed within the last thirty years, chiefly by the researches of Bunsen and Kirchhoff, the principles of which may here be shortly stated.

It has long been known that certain chemical substances, especially the salts of alkalis and alkaline earths, when strongly heated in the blowpipe, or other nearly colourless flame, impart to that flame a peculiar colour, by the occurrence of which the presence of the substance may be detected. If many of these substances are present together, the detection of each by the naked eye becomes impossible, owing to the colours being blended, and thus interfering with each other. Thus, for instance, the sodium compounds colour the flame an intense yellow, whilst the potassium salts tinge the flame violet: the yellow soda colour is, however, so much more intense than the purple potash tint, that a small trace of soda prevents the eye from detecting the purple, even if large quantities of potash salts are present. This difficulty is altogether overcome, and the method of observation rendered extremely sensitive, if, instead of regarding the flame with the naked eye, it is examined through a prism. This consists of a triangular piece of glass, in passing through which the light is refracted, or bent out of its course, each differently coloured ray being differently refracted: so that if a source of white light, such as the flame of a candle, is thus regarded, a continuous band of differently coloured rays is observed; the compound white light being resolved into all its variously coloured constituents. This coloured band is termed a *spectrum;* and each source of pure white light gives the same *continuous spectrum,* stretching from red (the least refrangible) to violet (the most refrangible) colour, identical in fact with the colours of the rainbow. (See No. 1 of the chromolith plate at beginning of volume.)

If these coloured flames are examined by means of a prism, the light being allowed to fall through a narrow slit upon the prism, it is at once seen that the light thus refracted differs essentially from white light, inasmuch as it consists of only a particular set of rays, each flame giving a spectrum containing a few *bright bands.* Thus the spectrum of the yellow soda flame contains only one fine bright yellow double line, whilst the purple potash flame exhibits a spectrum in which there are two bright lines, one lying at the extreme red, and the other at the extreme violet end. (See Nos. 7 and 2 on the above plate.) These peculiar lines are always produced by the same chemical element, and by no other known substance; and the positions of the lines always remain unaltered. When the spectrum of a flame tinted by a mixture of sodium and potassium salts is examined, the yellow ray of sodium is found to be confined to its own position, whilst the potassium red and purple lines are as plainly seen as they would have been had no sodium been present.

The coloured flames which are exhibited by the salts of lithium, barium, strontium, and calcium, likewise each give rise to a peculiar spectrum, by means of which the presence or absence of very small quantities of these substances in a mixture can be ascertained with certainty, simply by observing the presence or absence of the peculiar bright bands characteristic of the particular body. (See chromolith.)

The advantage which this new method of analysis possesses over the older processes lies in the extreme delicacy as well as in the great facility with which the presence of

TABLE SHOWING THE GROUPING OF THE ELEMENTS, OR THE PERIODIC SYSTEM OF THE ELEMENTS (*Mendeléeff*).

Groups.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series.	— R_2O	— R_2O_2 or $R\,O$.	— R_2O_3 —	$R\,H_4$ R_2O_4 or $R\,O_2$	$R\,H_3$ R_2O_5	$R\,H_2$ R_2O_6 or $R\,O_3$	$R\,H$ R_2O_7	(R_2H) Hydrogen Compounds. R_2O_8 or RO_4 } Higher Oxygen Compounds.
1	1 H							
2	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35·5 Cl	
4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56. Co 59. Ni 59.
5	63 Cu	65 Zn	69 Ga	73 Ge	75 As	78 Se	80 Br	
6	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—	Ru 104. Rh 104. Pd 106.
7	108 Ag	112 Cd	114 In	118 Sn	120 Sb	125 Te	127 I	
8	Cs 133	Ba 137	La 138	Ce 140	Di 142	—	—	— — —
9	—	—	—	—	—	—	—	
10	—	—	Yb 173	—	Ta 182	W 184	—	Os 191. Ir 193. Pt 195.
11	197 Au	200 Hg	204 Tl	207 Pb	208 Bi	—	—	
12	—			Th 234	—	U 239	—	

We can thus arrange the whole of the elements in groups of seven, as shown in the table, except that in three cases we have three elements with atomic weights nearly alike forming an eighth division of a group. In the vertical series we find the various groups of naturally allied elements, such as the alkali-metals, carbon group, nitrogen group, &c., whilst in the horizontal series the properties change regularly from one group to another. This is seen not only in the chemical properties, such as their power of combination with the maximum number of atoms of oxygen or hydrogen, but also in many of their physical properties. Thus the specific gravity of the series beginning with silver is as follows:

	Ag	Cd	In	Sn	Sb	Te	I
Sp. Gr. =	10·5	8·65	7·42	7·29	6·7	6·25	4·95.

It appears, therefore, that matter becomes endowed with similar properties when the atomic weight has increased by 16, 33, or 50 units, or in other words *the properties of the elements are periodic functions of the atomic weights.* This was first enunciated by Newlands, and afterwards more thoroughly worked out by the Russian chemist Mendeléeff, and by Lothar Meyer, and is known as *the periodic law.*

Further examination of the table shows that other relationships exist between many of the elements: thus it frequently happens that the elements of one vertical group are connected by isomorphism or by analogous chemical properties with those in a neighbouring horizontal series. Thus vanadium, showing its close connection with phosphorus by its volatile oxychloride and by the isomorphism of the vanadates with the phosphates, is allied in its chemical characters with niobium and also with chromium and molybdenum.

These last two elements are connected with sulphur by the isomorphism of the chromates, molybdates, and sulphates, just as manganese and chlorine are connected by the isomorphism of the permanganates and the perchlorates. Silver, on the one hand, exhibits analogies with copper and mercury, but, on the other, the isomorphous relations which it exhibits to sodium place it near the metals of the alkalis.

Prediction of New Elements. In the above table a number of gaps will be noticed where there is no element known

TABLE SHOWING THE GROUPING OF THE ELEMENTS, OR THE PERIODIC SYSTEM OF THE ELEMENTS (*Mendeléeff*).

Groups.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series.	— R_2O	— R_2O_2 or RO.	— R_2O_3 —	RH_4 R_2O_4 or RO_2	RH_3 R_2O_5	RH_2 R_2O_6 or RO_3	RH R_2O_7	(R_2H) Hydrogen Compounds. R_2O_8 or RO_4 } Higher Oxygen Compounds.
1	1 H							
2	Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
3	23 Na	24 Mg	27 Al	28 Si	31 P	32 S	35·5 Cl	
4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56. Co 59. Ni 59.
5	63 Cu	65 Zn	69 Ga	73 Ge	75 As	78 Se	80 Br	
6	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	—	Ru 104. Rh 104. Pd 106.
7	108 Ag	112 Cd	114 In	118 Sn	120 Sb	125 Te	127 I	
8	Cs 133	Ba 137	La 138	Ce 140	Di 142	—	—	— — —
9	—	—	—	—	—	—	—	
10	—	—	Yb 173	—	Ta 182	W 184	—	Os 191. Ir 193. Pt 195.
11	197 Au	200 Hg	204 Tl	207 Pb	208 Bi	—	—	
12	—			Th 234	—	U 239	—	

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Prediction of New Elements. In the above table a number of gaps will be noticed where there is no element known

metallic spectrum be both allowed to fall, one below the other, in the field of the telescope, the bright lines of the metal are *all* seen to be continued in dark solar lines. In the case of metallic iron alone, more than sixty such coincidences have been observed ; and the higher the magnifying power employed, the more striking and exact does this coincidence appear.

With other metals—such, for instance, as gold, antimony, lithium—no single coincidence can be noticed, whilst all the lines of certain other metals have their dark representatives in the sun. From these facts it is clear that there must be some kind of connection between the bright lines of these metals and the coincident dark solar lines, as such coincidences cannot be the result of mere chance. Is the coincidence of the *dark* solar lines with the *bright* iron lines caused by the presence of iron in the sun? And if so, how do the lines come to appear *dark* in the solar spectrum?

The explanation of this is given by an experiment, in which the bright metallic lines are *reversed*, or changed into dark lines. Thus the bright yellow soda lines (coincident with Fraunhofer's lines D) can be made to appear as dark lines, by allowing the rays from a strong source of white light (such as the oxyhydrogen light) to pass through a flame coloured by soda, and then to fall upon the slit of the spectroscope. Instead of then seeing the usual soda spectrum of a *bright* yellow double line upon a dark ground, a double *dark* line, identical in position and breadth with the soda line, will be seen to intersect the continuous spectrum of the white light. Here then the yellow flame has absorbed the same kind of light that it emits, a consequent diminution of intensity in that part of the spectrum has occurred, and a dark line has made its appearance. In like manner the spectra of many other substances have been *reversed*, each substance in the state of vapour having the power of absorbing the same rays it emits, or being opaque for such rays.

The explanation of the existence of dark lines in the solar spectrum, coincident with bright metallic lines, now becomes evident : these dark lines are caused by the passage of white light through the glowing vapour of the metals in question, present in the sun's atmosphere, and these vapours absorb exactly the same kind of light which they are able to emit.

The sun's atmosphere, therefore, contains these metals in the condition of glowing gases, the white light proceeding from the strongly heated solid or liquid mass of the sun which lies in the interior.

By observing the coincidences of these dark lines with the bright lines of terrestrial metals, we arrive at a knowledge of the occurrence of such metals in the solar atmosphere with as great a degree of certainty as we are able to attain in any question of physical science. The metals hitherto detected in the sun's atmosphere are seventeen in number, viz. iron, sodium, potassium, magnesium, calcium, chromium, nickel, barium, copper, zinc, strontium, cadmium, cobalt, manganese, aluminium, lead, titanium. Hydrogen and oxygen are also known to exist in the sun. The former element is found to exist in large quantity surrounding the luminous portions of the sun's body as a zone of incandescent gas, termed the solar *chromosphere*, whilst masses of ignited hydrogen thrown still higher form the red protuberances seen during a total eclipse. The rapidity with which the ignited hydrogen moves on the sun's surface is enormous; solar cyclones or circular storms have been shown by Lockyer to blow with a velocity compared with which our most violent terrestrial tornadoes are mere summer breezes.

Stellar Chemistry.—The same methods of observation and reasoning apply to the determination of the chemical constitution of the atmospheres of the fixed stars, which are self-luminous suns; but the experimental difficulties are greater, and the results, therefore, are as yet less complete, though not less conclusive than is the case with our sun.

The spectra of the stars all contain dark lines, but these are for the most part different from the solar lines, and differ from one another; hence we conclude that the chemical constitution of the solar and stellar atmospheres is different. Many of the substances known on this earth have been detected in the atmosphere of the stars. We owe this most important discovery to Dr. Huggins and Professor W.. A. Miller. Thus the star called Aldebaran contains hydrogen, sodium, magnesium, calcium, iron, tellurium, antimony, bismuth, and mercury; whilst in Sirius only sodium, magnesium, and hydrogen have with certainty been detected.

In examining the spectra of some of the nebulæ, a striking difference is observed : the stellar spectra, it will be remembered, resemble the spectrum of the sun, inasmuch as each consists of a *bright* ground intersected with *dark* lines ; the spectra of certain of the nebulæ, on the other hand, consist simply of *bright lines*, like the spectra of hydrogen, nitrogen, or any of the metals. Hence we conclude that these nebulæ are masses of glowing gas, and do not consist, like the sun and stars, of a solid or liquid mass, surrounded by a gaseous atmosphere.

The subject of solar and stellar chemistry is still in its infancy, but the results already obtained lead to the belief that our knowledge of the chemical composition of those far distant bodies will become more intimate as the methods of experiment and observation are gradually perfected.

[For fuller information on this subject see Roscoe's *Lectures on Spectrum Analysis*, and Lockyer's *Lessons in Elementary Astronomy*.]

CHEMISTRY OF THE CARBON COMPOUNDS OR ORGANIC CHEMISTRY

LESSON XXVIII

ORGANIC CHEMISTRY has been defined as the chemistry of the carbon compounds, as carbon forms the most important and characteristic constituent of vegetable and animal substances. It was formerly believed that these compounds could not be obtained artificially, but that for their formation life in some form or other was necessary. This view has however long since been proved incorrect, and it is now known that no real difference exists in the laws regulating the formation of the substances classed under these two great divisions. Nevertheless the number of compounds which belong to this group is so large, and their constitution frequently sc complicated, that they are best considered after the more simple inorganic compounds have been described. Carbon itself, however, as well as the more simple carbon compounds, such as the oxides and the carbonates, are for the sake of convenience always considered together with the inorganic compounds. (See p. 75.)

A distinction must be carefully drawn between an *organic* substance and an *organism;* the former is a single and definite substance which it is possible to prepare artificially from its elementary constituents; the latter contains several or many definite chemical substances and has a form, the result of animal or vegetable growth, which cannot be produced by artificial means. It does, indeed, differ fundamentally in constitution and mode of formation from any inorganic compound, inasmuch as it exhibits what is termed an *organised* structure, being the sole and direct product of animal or vegetable life. Such an organised structure is seen in the simple *cell,* the germ of living organisms. It cannot be artificially prepared from its elementary constituents, whereas any crystalline or liquid organic body may possibly be thus built up from its elements.

The first striking peculiarity which the carbon compounds exhibit is their extraordinary number, those already known far exceeding all the compounds of the other elements taken together, and new ones being daily brought to light. A second peculiarity of these compounds is, that the great majority of them are formed by the union of carbon in different proportions with one or more of three other elements, viz., hydrogen, oxygen, and nitrogen; whilst the number of *atoms* of these elements contained in the *molecule* of many organic bodies is extremely large; thus sugar contains 45, and stearin no less than 173 atoms of the constituent elements.

The cause of the multiplicity of the carbon compounds is to be found in a fundamental and distinctive property of carbon itself. This consists in the power which this element possesses, in a much higher degree than any of the others, of *uniting with itself* to form complicated compounds, containing an aggregation of carbon atoms united with either hydrogen, oxygen, nitrogen, or several of these, bound together to form a distinct chemical whole.

Carbon is a tetratomic element; the simplest compound of carbon with hydrogen is marsh gas or methane, CH_4.

In this compound the *four combining units* of the carbon atom are saturated, or satisfied, by union with the four atoms of hydrogen; and hence marsh gas, CH_4, is said to be a *saturated compound.* Four atoms of any other monad would, however, satisfy this condition; and we find, in fact, that one or more of the four atoms of hydrogen can be substituted, step by step, for chlorine, so that the following *substitution products* are obtained:

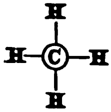
$$CH_4. \quad CH_3Cl. \quad CH_2Cl_2. \quad CHCl_3. \quad CCl_4.$$

The four combining units of the carbon atom can be saturated not only by the union of the carbon to four monad atoms, but also by its union to two dyad atoms, or to one triad and one monad, or to one tetrad atom. Thus in carbon dioxide, CO_2, and carbon disulphide, CS_2, we have a carbon atom saturated with two dyads: in hydrogen cyanide (prussic acid), CHN, we have a carbon atom saturated with a triad (N) and a monad (H) element.

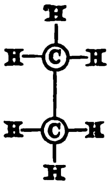
When two atoms of tetravalent carbon unite together, a new radical or group of atoms is formed: the simplest case of this *duplication* of the carbon element is that of the combination of one of the four combining units of one atom with one of the four units of the other atom: so that two of the *eight* original combining units are saturated or disposed of, and only *six* remain free to combine. Hence, whilst CH_4 is the type and starting point of the monocarbon series, C_2H_6 is that of the dicarbon series; and similarly, C_3H_8 that of the tricarbon series; and no compound of any of these three series is known containing respectively more than four, six, or eight atoms of a monad.

The following graphic representation of these three typical compounds may help to render their mode of formation more evident—

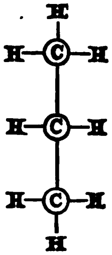
Monocarbon Series.



Dicarbon Series.



Tricarbon Series.



If four atoms of carbon combine together in a similar manner, ten combining units remain free and yield on saturation with hydrogen the hydrocarbon C_4H_{10}, and so on. It will thus be seen that a substitution of an atom of hydrogen by the group CH_3 is necessary to pass up the series, or in other words each of these hydrocarbons differs from the previous one by containing in addition the elements CH_2, and the composition of the members of the series may therefore be represented by the general formula $C_nH2n + 2$.

The replacement of an atom of hydrogen by the group CH_3

can actually be experimentally made, and the higher and more complicated carbon compounds thus obtained by *synthesis* from the lowest and simplest one, whilst this, in its turn, can be prepared from its constituent elements. We are well acquainted with a large number of artificially prepared members of this series, containing from one to fifteen atoms of carbon, combined with a saturating quantity of hydrogen; and each member of the series forms a starting-point for a number of peculiar derivatives all containing a common constituent, and exhibiting a family likeness.

Homologous Series. Compound Radicals.—The compounds obtained from each member of this ***homologous series*** of mono-, di-, tri-, and higher carbon groups, may indeed be compared with those of the inorganic metals; and each different carbon series may be supposed to contain a group of atoms of carbon and hydrogen which plays the same part in these compounds as the metal does in the metallic salts, and to which the name of *compound radical* has been given. An example of such a compound radical has also been described in the inorganic portion, viz. *Ammonium* (p. 199). The radical contained in each of the three typical substances whose formulæ are given on p. 277, consists of carbon and hydrogen atoms, and contains one atom less hydrogen than the hydrocarbon itself; and each of these bodies may therefore be termed the *hydride* of a radical, and considered to be a molecule of hydrogen, $\left.\begin{matrix}H\\H\end{matrix}\right\}$, in which one atom of the hydrogen is replaced by a radical. Thus we have:

Monocarbon Series.	Dicarbon Series.	Tricarbon Series.
Methyl hydride or Methane $\left.\begin{matrix}CH_3\\H\end{matrix}\right\}$	Ethyl hydride or Ethane $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$	Propyl hydride or Propane $\left.\begin{matrix}C_3H_7\\H\end{matrix}\right\}$

By replacing one of the hydrogen atoms in the hydrocarbon by chlorine, we obtain a corresponding *chloride;* viz.:

Monocarbon Series.	Dicarbon Series.	Tricarbon Series.
Methyl chloride $\left.\begin{matrix}CH_3\\Cl\end{matrix}\right\}$	Ethyl chloride $\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$	Propyl chloride $\left.\begin{matrix}C_3H_7\\Cl\end{matrix}\right\}$.

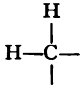
And by replacing a hydrogen atom by the monatomic radical hydroxyl, OH, in each hydride, we obtain an important class of bodies termed *alcohols:*

Monocarbon Series.	Dicarbon Series.	Tricarbon Series.
Methyl alcohol $\left.\begin{matrix}CH_3\\HO\end{matrix}\right\}$	Ethyl alcohol $\left.\begin{matrix}C_2H_5\\HO\end{matrix}\right\}$	Propyl alcohol $\left.\begin{matrix}C_3H_7\\HO.\end{matrix}\right\}$

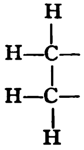
The radicals, *methyl*, CH_3, *ethyl*, C_2H_5, and *propyl*, C_3H_7, in these several compounds remain indivisible throughout all the derivatives, and give the peculiar characters to each series.

Polyvalent Radicals.—As in mineral chemistry we have radicals (see p. 164), some of which are monads, and some dyads, triads, or tetrads, so amongst the carbon compounds many radicals exist in which more than one combining unit remains unsaturated, and which therefore act as *polyvalent radicals:* thus methylene, $\overset{II}{CH_2}$, and ethylene, $\overset{II}{C_2H_4}$, are dyads, each containing two atoms of hydrogen less than the corresponding saturated hydrocarbon; whilst propenyl, $\overset{III}{C_3H_5}$, is a triad, containing three atoms of hydrogen less than propyl hydride or propane.

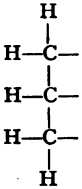
These radicals may be represented by the graphic formulæ.



Methylene



Ethylene



Propenyl.

They give rise to a large class of derivatives, each containing the radical or group of carbon and hydrogen atoms. Thus we have from the dyad radicals :

Ethylene chloride	$C_2H_4\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$;	Ethylene alcohol	$C_2H_4\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.
Propylene chloride	$C_3H_6\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$;	Propylene alcohol	$C_3H_6\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.

Whilst the triad radical propenyl yields the following:

Trichlorhydrin, or Propenyl Trichloride.	$C_3H_5\left\{\begin{matrix}Cl\\Cl\\Cl\end{matrix}\right.$;	Glycerine, or Glycerol	$C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$.

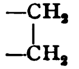
Tetrad, pentad, and hexad hydrocarbon radicals are also known, the derivatives of which are of great importance.

Besides the series of hydrocarbons having the general formula C_nH_{2n+2}, series are also known having the composition C_nH_{2n} and C_2H_{2n-2}, the members of which therefore contain respectively two and four atoms of hydrogen less than the corresponding members of the first series with the same number of carbon atoms, as will be seen at once from the following table:

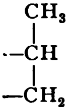
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
CH_4 Methane	—	—
C_2H_6 Ethane	C_2H_4 Ethylene	C_2H_2 Acetylene
C_3H_8 Propane	C_3H_6 Propylene	C_3H_4 Allylene
C_4H_{10} Butane	C_4H_8 Butylene	C_4H_6 Crotonylene
&c.	&c.	&c.

The members of the last two series are capable of combining directly with additional atoms of hydrogen and are therefore termed "unsaturated" compounds. They possess the characteristic property of combining directly with other elements in such quantity as to fill up the vacant combining powers. Thus ethylene or olefiant gas and acetylene combine with chlorine forming the compounds $C_2H_4Cl_2$ and $C_2H_2Cl_4$, whilst chlorine can only be introduced in the molecule of ethane by the simultaneous elimination of hydrogen.

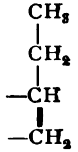
The constitution of the members of the C_nH_{2n} is represented by the following graphic formulæ:



$$\begin{array}{l} -CH_2 \\ \;\;| \\ -CH_2 \end{array}$$

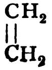


$$\begin{array}{l} \;\;CH_3 \\ \;\;\;| \\ -CH \\ \;\;\;| \\ -CH_2 \end{array}$$

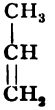


$$\begin{array}{l} \;\;CH_3 \\ \;\;\;| \\ \;\;CH_2 \\ \;\;\;| \\ -CH \\ \;\;\;| \\ -CH_2 \end{array}$$

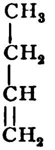
It is always found that in these hydrocarbons the combining units which are apparently free are attached to adjacent carbon atoms, as shown in the above formulæ, and it is therefore usually supposed that instead of the two combining units being actually free, the two adjacent carbon atoms are united by two instead of by one combining unit; the above formulæ then become:



$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array}$$



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$



$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ CH \\ \| \\ CH_2 \end{array}$$

Similarly in acetylene it is supposed that the two adjacent carbon atoms are united by three combining units, as in the formula

$$\begin{array}{c}CH\\ |||\\ CH\end{array}$$

Carbon monoxide, CO, must also be regarded as an unsaturated compound, for it unites directly with chlorine forming $COCl_2$, whilst carbon dioxide, CO_2, forms no such additive products.

Fatty Group of Organic Compounds.—All the substances derived by addition or substitution from the foregoing series of hydrocarbons are known as fatty or aliphatic compounds, because the acids which occur in most vegetable and animal fats belong to this series.

Aromatic Group of Organic Compounds.—The compounds belonging to the aromatic group all contain a group of carbon atoms united together in the form of a closed chain, or are derived from compounds containing a similar chain of carbon atoms and nitrogen or other atoms. The name "aromatic" was given to this group, because those members which were first examined all possessed an aromatic taste or smell.

From what has been said above with regard to the building up of the hydrocarbons, and the substitution of other elements or groups for hydrogen, it will be seen that a new and perhaps more correct definition than that above given of organic chemistry is possible, viz., that it is "The Chemistry of the Hydrocarbons and their derivatives."

Like the inorganic compound radicals, the hydrocarbon radicals, although they are unaltered in a large number of reactions, may under suitable conditions undergo alteration. In many cases the number and grouping of the carbon atoms remains unaltered, but the resulting radical is divalent or polyvalent instead of monovalent. For example, ethyl alcohol, a derivative of the monovalent radical ethyl, yields by loss of the elements of water the divalent ethylene:

$$C_2H_6O - H_2O = C_2H_4.$$

In other cases the reaction proceeds further, the group of carbon atoms being split up into two or more portions. Thus succinic acid on electrolysis yields carbon dioxide, ethylene and hydrogen:

$$C_4H_6O_4 = 2CO_2 + C_2H_4 + H_2$$

whilst on heating a salt of acetic acid with an alkali it yields carbon dioxide and methane :

$$C_2H_4O_2 = CH_4 + CO_2$$

On the other hand many reactions are known in which two organic radicals combine together forming compounds which behave as derivatives of a simple radical. Thus by replacing one atom of hydrogen in methane or marsh gas and by the monad methyl group, we obtain, as already mentioned (p. 277) the hydrocarbon ethane, C_2H_6; and if one of the hydrogen atoms in the latter be replaced by the ethyl group we obtain butane, C_4H_{10}.

Further we may replace one atom of hydrogen in methane by chlorine, forming methyl chloride, CH_3Cl, the chlorine of which may in turn be replaced by cyanogen, CN ; the compound obtained, CH_3CN, behaves no longer as a methyl derivative, the carbon atoms being combined in the same way as in the ethyl derivatives, into some of which it may be readily converted.

These examples give an indication of the method by which it has been found possible to prepare compounds rich in carbon from such as contain only one carbon in the molecule.

Law of Even Numbers.—It is found that, in whatever manner the carbon atoms may be united together, the combining units which remain unsaturated are an even number : from this and from the tetravalent character of carbon it follows that the sum of the atoms of monad or triad elements united with the carbon must be an even number, whilst the number of dyad elements is not thus restricted.

We shall first study the properties and mode of formation of some of the most important members of the fatty group, and then notice the chief properties of the aromatic series of organic bodies. Before doing so, it is, however, necessary to place before the student some general considerations. The first of these relates to

Empirical and Constitutional Formulæ.

The simplest mode of expressing the composition of an organic compound is to write down the number of the constituent atoms side by side, thus :

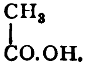
C_2H_6	Ethane,
C_2H_6O	Ethyl alcohol,
C_2H_7N	Ethylamine,
$C_2H_4O_2$	Acetic acid.

These expressions represent the *molecular weights* of the substances, and are called *empirical* or *molecular formulæ.* Amongst the very large number of carbon compounds, it happens not unfrequently that two or more organic bodies possess the same chemical composition (that is, they contain the same number of atoms of the same elements in the molecule), although they differ in their chemical and physical properties. In order to distinguish between these *isomeric* bodies, it is necessary to employ *constitutional formulæ*, for the purpose of giving an idea of the chemical nature of the substances, or representing the decompositions which they undergo. The foregoing compounds can be represented by the following constitutional formulæ :

Ethane, $C_2H_5.H$; Ethyl alcohol, $C_2H_5.OH$.
Ethylamine, $C_2H_5.NH_2$; Acetic Acid, $C_2H_3O.OH$.

This denotes that the monad radical C_2H_5 is contained in the first three compounds ; that alcohol may be regarded as water in which one atom of hydrogen has been replaced by ethyl, and that ethylamine stands in the same relation to ammonia. The formula for acetic acid shows that it may be considered to be alcohol in which two atoms of hydrogen are replaced by one atom of oxygen, and that one atom of hydrogen is differently placed from the other three.

A constitutional formula, may, however, be of different degrees of completeness ; thus, for instance, it is frequently useful to represent acetic acid by the formula : (see p. 314)—



$$\begin{array}{l} CH_3 \\ | \\ CO.OH. \end{array}$$

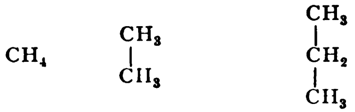
This signifies that acetic acid contains two atoms of carbon attached together (this is shown by the straight line), of which one is connected with three atoms of hydrogen, and the other with dyad oxygen O, and the monad hydroxyl OH.

It is important to remember that the formula does not point out the actual mode in which the atoms in the molecule are connected together, but simply indicates the deportment of the compound. We shall in the future have frequent occasion to employ both empirical and constitutional formulæ of different kinds for the same substance, according to the nature of the reaction or peculiar property which we desire to explain.

Isomerism.

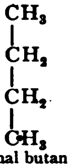
Carbon compounds having the same percentage composition, which differ in their chemical and physical properties, are said to be *isomeric*. The isomerism of such bodies may be due to several causes:

(1) *Isomerism in the restricted sense* refers to compounds which contain the same number of atoms in the molecule. In the series of hydrocarbons, having the general formula, C_nH_{2n+2}, cases of isomerism can only arise from a different mode of arrangement of the carbon atoms. The first three terms of this series do not possess any isomerides:



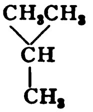
$$CH_4 \qquad \begin{array}{c}CH_3\\ |\\ CH_3\end{array} \qquad \begin{array}{c}CH_3\\ |\\ CH_2\\ |\\ CH_3\end{array}$$

The fourth term, C_4H_{10}, is derived from the third by the replacement of one atom of hydrogen by the group CH_3; this replacement can, however, take place either with one of the atoms of hydrogen attached to the atoms of carbon lying at the end of the chain, or with one of the atoms of hydrogen attached to the central atom of carbon, and we thus obtain the isomerides:



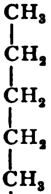
Normal butane.

and

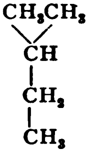


Isobutane.

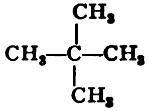
Of the next term three isomerides can exist:



Normal pentane.



Isopentane.

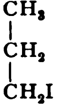


Mesopentane.

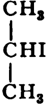
In the higher members of this series the possible number of isomerides rapidly increases.

The compounds of the fatty group can be derived from these hydrocarbons by the replacement of one or more atoms of hydrogen by other elements or groups of atoms, and according as this replacement takes place in connection with one or other of the carbon atoms, so will cases of isomerism arise. The following examples illustrate some of the more simple cases:

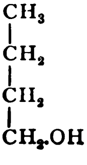
Propyl Iodide.



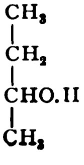
Iso-propyl Iodide.



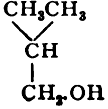
Normal Butyl Alcohol.



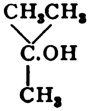
Secondary Butyl Alcohol.



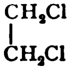
Fermentation Butyl Alcohol.



Tertiary Butyl Alcohol.

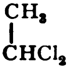


Ethylene Chloride.



$$\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

Ethidene Chloride.



$$\begin{array}{c} CH_3 \\ | \\ CHCl_2 \end{array}$$

With unsaturated compounds a still larger number of isomerides is possible, inasmuch as the hydrogen atoms may be wanting in different positions. Isomerism in the aromatic series is produced by the same causes as in the paraffin group of bodies, and also by another cause which will be explained afterwards (see Orientation in the benzene ring).

(2) *Polymerism.*—Compounds possessing the same percentage composition, but having different molecular weights, are termed polymeric; thus a series of polymeric hydrocarbons is known which contains double as many atoms of hydrogen as of carbon:

Ethylene	C_2H_4
Propylene	C_3H_6
Butylene	C_4H_8
Amylene	C_5H_{10}

The following compounds are also polymers:

Aldehyde	C_2H_4O
Paraldehyde	$C_6H_{12}O_3$

(3) *Metamerism.*—Bodies possessing the same percentage composition and the same molecular weight may also be formed by the occurrence of different radicals united into one whole by an atom of such an element as oxygen, nitrogen, sulphur, &c., making up the same total number of atoms, but giving rise to different compounds. Out of the large number of such metameric bodies, the following may serve as examples:

Propylamine.

$$N\left\{\begin{array}{l} C_3H_7 \\ H \\ H \end{array}\right.$$

Methylethylamine.

$$N\left\{\begin{array}{l} CH_3 \\ C_2H_5 \\ H \end{array}\right.$$

Trimethylamine.

$$N\left\{\begin{array}{l} CH_3 \\ CH_3 \\ CH_3 \end{array}\right.$$

Dipropyl Ether.

$$\left.\begin{array}{r} C_3H_7 \\ C_3H_7 \end{array}\right\}O$$

Methyl-amyl Ether.

$$\left.\begin{array}{r} CH_3 \\ C_5H_{11} \end{array}\right\}O$$

Ethyl-butyl Ether.

$$\left.\begin{array}{r} C_2H_5 \\ C_4H_9 \end{array}\right\}O$$

Butyric Acid.

$$\left.\begin{array}{r} C_4H_7O \\ H \end{array}\right\}O$$

Methyl Propionate.

$$\left.\begin{array}{r} CH_3 \\ C_3H_5O \end{array}\right\}O$$

Ethyl Acetate.

$$\left.\begin{array}{r} C_2H_5 \\ C_2H_3O \end{array}\right\}O$$

Propyl Formate

$$\left.\begin{array}{r} C_3H_7 \\ CHO \end{array}\right\}O.$$

LESSON XXIX

DETERMINATION OF THE COMPOSITION OF CARBON COMPOUNDS

1. *Organic Analysis. Estimation of Carbon and Hydrogen.*

As all organic compounds contain carbon, and most of them hydrogen, the estimation of these two constituents becomes a matter of importance, and the method of analysis remains nearly the same for all organic substances. It is founded upon the fact that when any compound of carbon is heated to redness with excess of oxygen, it undergoes complete combustion, the carbon being oxidised to carbon dioxide (carbonic acid), and the hydrogen to water, so that by weighing the quantity of these two products obtained by burning a given weight of the substance we can ascertain the weight of carbon and of hydrogen which the substance contained.

The combustion of the organic compound can either be made in a current of pure oxygen gas, or by mixing the body with pure copper oxide (CuO), which readily parts with its oxygen to hydrogen or carbon at a red heat, the products of combustion in either method being carefully collected and weighed. The method formerly adopted and still used to some extent is as follows: A weighed quantity (generally about 0·3 gram) of the solid substance about to be analysed by means of copper oxide is brought into a combustion tube made of hard Bohemian glass (AA, Fig. 70), about 50 to 60 centimeters in length, and drawn out at one end to a fine point, and open at the other. Before the introduction of the substance, a quantity of pure and perfectly dry, freshly-ignited, granulated, copper oxide is brought into the tube sufficient to fill about one quarter of its length, and the substance is well mixed with this oxide by means of a brass wire (B, Fig. 70); fresh oxide is then added, the brass wire being well cleaned from every possible trace of the adhering substance, until the tube is nearly filled.

The apparatus intended to collect the water produced is now attached to the open end of the tube by means of a well-fitting dry cork : it consists of a tube (C), filled with porous pieces of calcium chloride, and accurately weighed ; this substance effectually absorbs all the water and aqueous vapour formed in the combustion ; the carbon dioxide passes though the tube unabsorbed, and bubbles into a solution of strong caustic potash contained in the bulb apparatus (D), attached to the drying tube by a well-fitting caoutchouc joint (E). Connected with the potash-bulbs and weighed with them is another small drying tube (not shown in the figure) for the purpose of preventing any escape of moisture from the potash solution. The increase in weight of the drying tube (C), and of the potash-bulbs (D) gives respectively the weight of water and carbon dioxide produced.

The combustion tube is placed in a long furnace, so that it can be gradually heated to redness : this is most readily effected by a number of gas burners arranged in line, so that each part of the tube can be gradually and separately heated (F). A large number of small burners is placed under the part of the tube containing the substance, in order that the combustion may be more accurately regulated. After the whole arrangement has been shown to be properly air-tight, the part of the tube near the cork, containing only pure copper oxide, is heated ; and when a length of 15-20 centimeters of it is red hot, the part of the tube containing the substance is gently heated, until bubbles of carbonic acid are seen slowly to enter the potash-bulbs ; and the heat is applied so that this slow disengagement of carbonic acid continues until the whole of the substance is burnt.

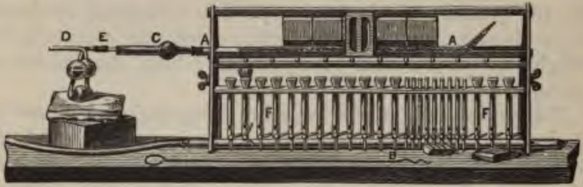


FIG. 70.

When the gas ceases to come off, the whole length of the tube is strongly heated for some minutes, and as soon as the potash solution begins to pass back into the bulb nearest the combustion-tube (owing to the absorption of the carbonic acid), the drawn-out end of the tube is broken, the gas flames extinguished at the end of the furnace, and dry air passed for some minutes through the whole apparatus by means of an aspirator. This operation is necessary, in order to collect in the potash the carbonic acid which still remains in the combustion-tube. As soon as this is finished, the analysis is complete with the exception of weighing the drying-tube and potash-bulbs. Many precautions must be taken, and much attention to details must be paid in order to ensure accurate results in organic analysis: for an enumeration of these the larger manuals must be consulted.

If the substance under examination is a liquid, it is sealed up in a small weighed glass-bulb drawn out to a fine point; this is again weighed, the point broken off, and the bulb dropped into the combustion-tube, and the operation conducted as above described. When nitrogen is contained in the body about to be analysed, it is necessary to place a spiral of copper gauze in the front part of the tube to decompose any nitrous fumes which are formed and would be absorbed by the potash, and thus impair the result.

The method above described is that employed by Liebig. At the present time a modified form of apparatus is usually employed, which allows a series of analyses to be made one after the other without disturbing the copper oxide (Fig. 71, 72).

The tube employed (Fig. 71), is open at both ends, and is filled in the following manner: at the right-hand end a space of 15-20 cm. is left free for the introduction of metallic copper if the substance to be analysed contains nitrogen, and the tube then filled for about 25-30 cm. with granulated copper oxide, which is retained in its position by

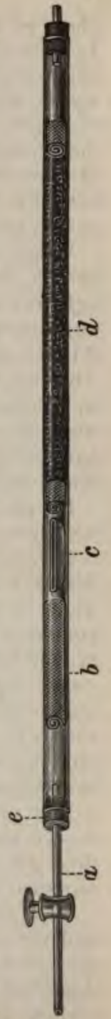


FIG. 71.

plugs of asbestos, or better, by small rolls of copper gauze. In front of the copper oxide is placed a platinum or porcelain boat containing a weighed amount of the substance to be analysed, and then a spiral of oxidized copper gauze about 10 cm. in length. The left-hand end of the tube is connected with the drying apparatus (Fig. 72 A) by means of which a current of pure air or oxygen gas can be passed continually over the heated substance. The aspirator (B) is placed in front of the potash bulbs to remove pressure from the apparatus.

When all is ready and the column of copper oxide well heated, the burners under the oxidized copper spiral are lighted, and afterwards those under the platinum boat gradually turned on, and at the same time a current of oxygen passed through until the whole of the substance is completely burned. The oxygen in the tube and potash-bulbs is then driven out by a current of dry air, and the drying tube and potash-bulbs weighed as before. As soon as the front part of the furnace has cooled down, another portion of substance can be introduced and analysed.

In place of potash-bulbs, tubes containing granulated soda-lime are frequently employed with satisfactory results.

2. *Determination of Nitrogen.*—Many nitrogenous organic bodies, when heated with caustic soda, or potash, yield the whole of the nitrogen which they contain in the form of ammonia. This evolution of ammonia is easily rendered evident by heating a small piece of cheese with solid caustic soda. Upon this reaction a method is based for determining the quantity of nitrogen in organic bodies: it consists simply in heating a given weight of substance with a mixture of caustic soda and quicklime in a tube, collecting in hydrochloric acid the ammonia formed, and estimating the weight of ammonium chloride produced by weighing as double platinum salt. For every 100 parts by weight of this salt obtained the substance contains 6·35 parts of nitrogen.

In many cases, however, this method is not applicable, and the nitrogen is now generally determined by heating the substance with copper oxide. A tube is filled, as described on p. 288, and the air expelled by passing carbon dioxide through the tube. The latter is then heated, and the gases produced passed over metallic

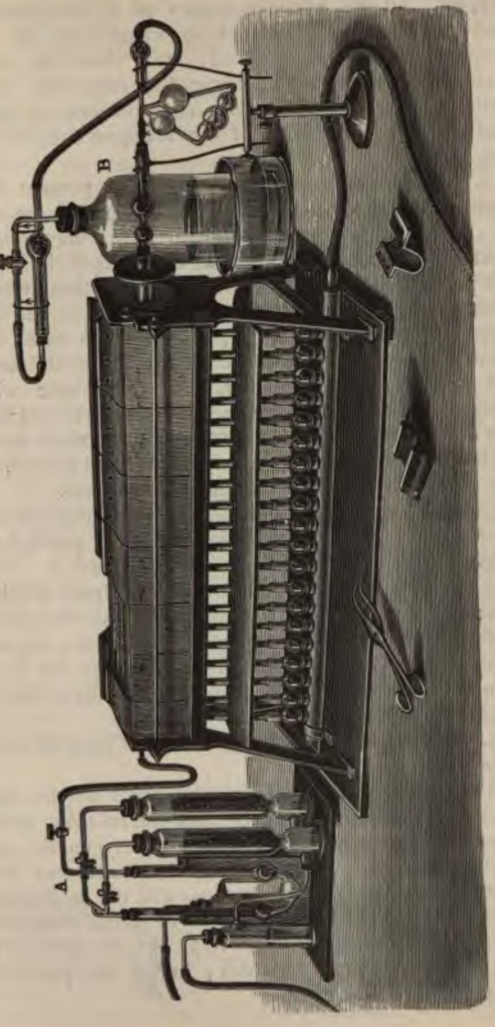


FIG. 72.

copper. All the nitrogen comes off in the gaseous form, and may be easily purified by caustic potash from the carbonic acid also evolved; and thus the volume of nitrogen obtained can be accurately measured. From this volume, measured under given circumstances of temperature and pressure, the weight of the nitrogen can, of course, be calculated.

3. *Chlorine, bromine and iodine* when present in organic substances are usually determined by heating the compound in a sealed tube at 150-250° with pure concentrated nitric acid and silver nitrate, when all the halogen is obtained as the insoluble silver salt. The pressure in these tubes is very great, and they must therefore be heated in the apparatus shown under ethane. (Fig. 76). In some cases it is preferable to heat the substance with pure quicklime, dissolve the product in nitric acid, and precipitate with silver nitrate. Sulphur and phosphorus are determined by heating the organic body with a mixture of pure nitre and sodium carbonate, placed in a tube; sulphuric and phosphoric acids are formed and estimated in the usual manner.

Sulphur may also be determined by heating the substance in a sealed tube with nitric acid, and precipitating the sulphuric acid formed with barium chloride.

4. *Oxygen* is usually obtained by difference—that is, by subtracting the sum of the weights of all the constituents which have been directly determined, from the weight of substance taken; several direct methods for the estimation of oxygen have been proposed, but these are not often used.

5. *Determination of the Molecular Weight of an Organic Compound.*

The above method of analysis gives us the percentage composition of the substance, and the *relation* between the number of atoms of carbon, hydrogen, oxygen, &c., contained in the compound, but we need to make a further determination in order to know the *formula* and the *molecular weight* of the body. Thus, in an analysis of glacial acetic acid, 0·395 gram of substance was found to yield 0·580 gram of carbonic acid, and 0·235 gram of water; hence 100 parts of glacial acetic acid consist of

Carbon	40·0	
Hydrogen . . .	6·6	
Oxygen	53·4	(by difference)
	100·0	

If we divide these numbers respectively by the combining weights of carbon, hydrogen, and oxygen, $\frac{40}{11·97} = 3·3$, $\frac{6·6}{1} = 6·6$, and $\frac{53·4}{15·96} = 3·3$, we obtain the relation between the combining weights of these constituents present. Thus we see that the number of atoms of carbon and oxygen is equal whilst that of hydrogen is twice as large : the composition of acetic acid is therefore represented by $C_nH_{2n}O_n$, but we do not know whether the true formula is CH_2O, $C_2H_4O_2$, or $C_3H_6O_3$, or whether it contains a still higher number of carbon atoms. In order to decide this point, and, therefore, to determine the *molecular weight* of the substance, we must endeavour to find a compound of it with some well-known element (such as silver), in which one atom of hydrogen is replaced by one atom of silver. On examination we find that only one compound of silver and acetic acid exists; and we find by experiment that 100 parts of silver acetate contain 64·68 parts by weight of silver; hence, the weight of the carbon, hydrogen, and oxygen, united with silver (Ag = 107·66), is $\frac{35·32 \times 107·66}{64·68} = 58·8$. In this silver acetate, however, one atom of hydrogen of the glacial acid was replaced by one of silver, so that the molecular weight of the glacial acetic acid is found to be $58·8 + 1 = 59·8$, or its formula is :

$$\begin{aligned} 2C &= 23·94 \\ 4H &= 4 \\ 2O &= 31·92 \\ \hline &\ 59·86 \end{aligned}$$

The slight difference observed between the found (59·8) and the calculated (59·86) molecular weight arises from unavoidable errors of experiment; the larger the number of analyses of the substance is made, the nearer will the mean result approach to the calculated numbers.

In a similar manner the molecular weights of organic bases are determined by ascertaining the weight of the substance which unites with a known weight of hydrochloric acid to form a salt. In the case of certain organic acids and bases, two or more compounds containing different proportions of silver (or other metal) and hydrochloric (or other) acid are known, and it becomes a matter for consideration which of these is to be taken as containing one molecule of the organic compound to one atom of metal or acid: the choice in these cases is determined by a consideration of the general properties of all the compounds. The latter method of decision also applies to many other bodies, such as sugar, turpentine, &c., which do not readily enter into combination with a metal or an acid.

There is one most important property by which the molecular weight of volatile organic bodies can be ascertained, viz. the *density* or *specific gravity of their vapours.* We have already seen that, in the case of the majority of gaseous and volatile inorganic compounds, Avogadro's hypothesis, which states that equal volumes of all gases contain the same number of molecules, may be used to determine the molecular weights of these compounds. The vapour density of water is 8·98, *i.e.* the weights of equal volumes of water-vapour and hydrogen, under like conditions of temperature and pressure, will be as 8·98 : 1. Now, as these volumes contain an equal number of the molecules of these bodies, the weight of the molecule of water must be 8·98 times the weight of the molecule of hydrogen. The weight of a molecule of hydrogen is assumed to be 2, and is represented by the formula H_2, so that the weight of a molecule of water is 17·96, or 2 × 8·98. By a similar process of reasoning the molecular weight of ammonia can be shown to be 17. What is true of these simple compounds in the gaseous state is true also of the more complex organic compounds under like conditions; and therefore, to determine the molecular weight of a volatile organic compound, all that is required is to determine its vapour density, *i.e.* the number of times a given volume of this substance in the gaseous state is heavier than an equal volume of hydrogen, to multiply the vapour density by two, and obtain in this way the molecular weight of the compound.

The experimental determination of the vapour densities of organic compounds thus becomes an important matter; for instance, the density of the vapour of acetic acid is found by experiment to be 30·07 (H = 1); and this accordingly gives a molecular weight to acetic acid of 60·14, a number agreeing with that obtained from purely chemical considerations (see *ante*, p. 293).

Another example may serve to render evident the importance of this relation : the combustion of acetal shows that the simplest relation of its constituent atoms is represented by the formula C_3H_7O ;[1] the determination of vapour density, however, gives the number 59·8 as the density of acetal gas : hence the molecular weight of acetal must be 59·8 × 2, and its formula not $C_3H_7O = 58·87$, but $C_6H_{14}O_2 = 117·74$. It is, of course, possible, when the molecular weight of a compound has been otherwise ascertained, to calculate its vapour density ; this calculated density will always differ slightly from that determined by experiment, owing to the unavoidable errors which occur : this, however, does not detract from the value of this method of controlling the molecular formula of a substance.

DETERMINATION OF VAPOUR DENSITY.

Two methods are employed for determining the vapour density of a compound. (1) By ascertaining the *weight* of a given volume of vapour. (2) By ascertaining the *volume* of a given weight of vapour. In the first of these processes, a thin glass globe is employed of about 200 to 300 cubic centimeters in capacity, having a finely drawn-out neck; the exact weight of the globe weighed in air and filled with dry air at a certain temperature and under an observed pressure having been found, a small portion of the substance whose density is to be determined is brought inside, and the globe then heated by plunging it into a water- or oil-bath (Fig. 73) raised to a temperature much above the boiling-point of the substance. As soon as the vapour has ceased to issue from the end of the neck, this end is hermetically sealed before a blowpipe, and the exact temperature as well as barometric pressure observed. The bulb thus filled with vapour is allowed to cool, and is next accurately weighed, and the point of the neck broken under mercury; the mercury rushes into the globe, owing to the vapour being condensed, and, if the experiment has been well conducted, completely fills it. From the volume of mercury which thus enters, the capacity of the globe is obtained.

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[1] We see that as this formula contains an uneven number of hydrogen atoms the existence of such a substance is impossible : we know that the true formula must be a multiple of this, which multiple we decide by the vapour density.

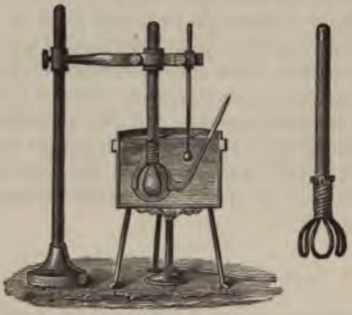


FIG. 73.

We have now all the data necessary for the determination. In the first place we have to find the weight of the given volume of the vapour under certain circumstances of temperature and pressure, and we then have to compare this with the weight of an equal volume of hydrogen gas measured under the same circumstances. The following example of the calculation of the vapour density of a volatile hydrocarbon may serve to illustrate the method: weight of globe filled with dry air at 15·5°, 23·449 grams; weight of globe filled with vapour at 110°, 23·720 grams; capacity of the globe, 178 cc. As the barometric column (760 mm.) underwent no change from the beginning to the end of the experiment, no correction for pressure is necessary. In order to get the weight of the vacuous globe, the weight of air contained must be deducted from the weight of globe in air. Now 1 cc. of air at 0° and 760 mm. weighs 0·001293 gram, and 178 cc. of air at 15°·5 would occupy $\frac{178 \times 273}{288\cdot5} = 168\cdot4$ at 0°, and the weight of this air is 0·218 gram: hence the weight of the vacuous bulb is 23·231, and the weight of vapour $23\cdot720 - 23\cdot231 = 0\cdot489$ gram. We must now find what 178 cc. of hydrogen at 110° will weigh; 1000 cc. of hydrogen at 0° weigh 0·0896 gram; 178 cc. at 100° will contract to 126·9 cc. at 0°. 126·9 cc. of hydrogen at 0° weigh 0·01137 gram; and this is therefore the weight of 178 cc. of hydrogen at 110°. Hence $\frac{0\cdot489}{0\cdot01137} = 43\cdot01$ is the density of the vapour, as found by experiment. The molecular weight of the substance therefore is 86. In this example many minor corrections, such as the expansion of the glass globe, the error of the mercurial thermometer, &c., are not considered; the above method gives results which are sufficiently accurate when the object is to control the molecular weight of a compound.

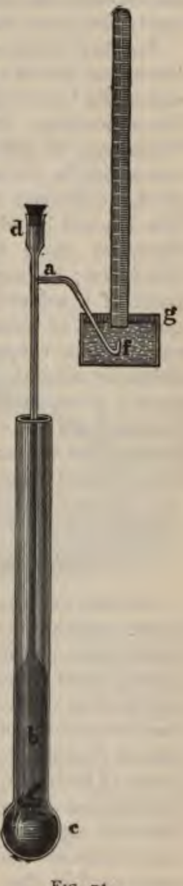


Fig. 74.

The second method of vapour density determination consists in ascertaining the volume occupied by a given weight of substance when heated up to a temperature considerably above its boiling-point. The mode of calculation is in principle the same as that of the former method.

Another process, simpler than either of the foregoing, known as Victor Meyer's method, is conducted as follows: the glass vessel (*b*), Fig. 74), filled with air, is heated by the vapour of water, or other liquid, placed in the bulb tube (*c*), until no more air is observed to pass out of the gas-delivery tube (*a*). The cork (*d*) is then removed, and the weighed quantity of the substance whose vapour density is required is dropped into the tube (*b*), the cork quickly inserted, and the displaced air collected in a graduated tube. From the volume of this air the vapour density can readily be calculated. For the details of manipulation the reader must refer to the larger manuals.

Another method of determining the molecular weight, known as Raoult's method, has of late been much employed, especially for compounds which cannot be volatilized without decomposition. It depends upon the following hypothesis: "Solutions of different substances in the same liquid, and containing in the same volume an equal number of molecules of the dissolved substance have the same freezing-point." The amount by which the freezing-point is lowered depends therefore upon the molecular weight of the dissolved substance; having once determined how much the freezing-point of a solvent is lowered by the addition of certain quantities of substances of known molecular weight, we can ascertain approximately the molecular weight of an unknown substance by finding what lowering of the freezing-point a given weight of it causes in that solvent. The results obtained are not so reliable as those obtained from the vapour density, but the method has proved very valuable when the latter cannot be ascertained.

Boiling-Point and Fractional Distillation.

Another important physical constant of organic compounds is the boiling-point. Every volatile chemical compound has, under given circumstances of pressure, a fixed and constant boiling-point; and this property is useful in ascertaining the purity of an organic liquid, as well as enabling us to separate the constituents of a mixture by means of fractional or continued distillation. The boiling-point of the *homologous* series of hydrides, alcohols, chlorides, &c. (p. 279), rises with the increase of carbon, and frequently proportionally to this increase, although no general law connecting boiling-point and chemical composition can be expressed. The arrangement used in the separation of liquids boiling at different points by means of fractional distillation is represented in

Fig. 75. The large surface presented by the wide tube in which the bulb of the thermometer is placed allows the vapour of the less volatile constituents to condense and flow back into the flask containing the mixture; the temperature of the vapour is indicated by the thermometer, and as the temperature rises beyond a given point, say from 5° to 5°, the liquid already distilled over is removed and an empty flask substituted to collect the portion of liquid next coming over. Each of these portions is next separately submitted to the same operation, and the process repeated until a pure substance with a constant boiling-point is obtained.

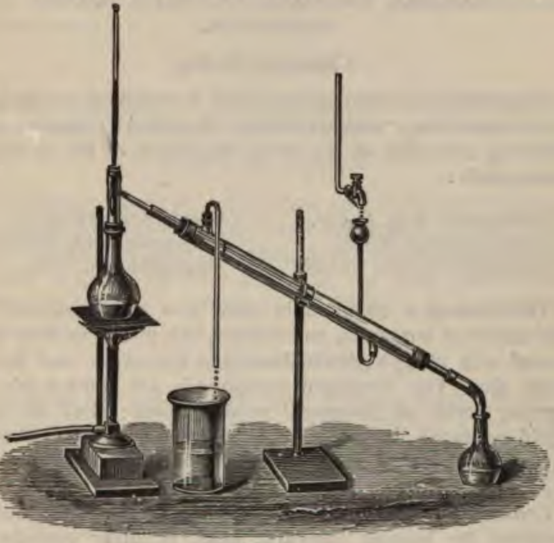


FIG. 75.

Many substances which undergo decomposition when boiled under the ordinary atmospheric pressure, can he distilled unchanged if the pressure is reduced. Hence substances must frequently be fractionated in vacuo.

LESSON XXX

CYANOGEN, CARBONYL, AND THIO-CARBONYL COMPOUNDS.

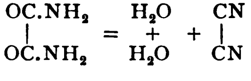
Cyanogen Series.

WE have already seen (p. 95) that a series of compounds exists containing a monad radical, CN, called *Cyanogen*. The following are some of the most important of the cyanogen compounds:

Hydrocyanic Acid, H.CN.	Cyanic Acid, HO.CN.
Cyanogen Gas, CN.CN.	Thiocyanic Acid, HS.CN.
Cyanogen Chloride, Cl.CN	Cyanamide $NC.NH_2$.

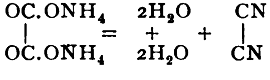
The cyanogen compounds may also be considered as derivatives of ammonia, and further, this group is also connected with other series of bodies as the oxalic and formic acids, &c. The cyanogen compounds are remarkable for forming series of *polymeric* modifications: thus we have liquid cyanogen chloride, CNCl, and solid cyanogen chloride, $C_3N_3Cl_3$; cyanic acid, HO.CN, and cyanuric acid, $H_3O_3C_3N_3$.

Cyanogen Gas, Dicyanogen, CN.CN.—This substance is obtained by heating mercury, gold, or silver cyanide; it is found in small quantities in the gases of the iron blast furnace. Its properties have already been mentioned (p. 97). It is also formed by the action of heat on oxamide, and ammonium oxalate, thus:



$$\begin{array}{l} OC.NH_2 \\ | \\ OC.NH_2 \end{array} = \begin{array}{c} H_2O \\ + \\ H_2O \end{array} + \begin{array}{l} CN \\ | \\ CN \end{array}$$

and



$$\begin{array}{l} OC.ONH_4 \\ | \\ OC.ONH_4 \end{array} = \begin{array}{c} 2H_2O \\ + \\ 2H_2O \end{array} + \begin{array}{l} CN \\ | \\ CN \end{array}$$

and is thus connected with the oxalic group, as cyanogen is oxamide, minus two molecules of water, and is the nitrile of oxalic acid. Cyanogen gas forms with potash a mixture of potassium cyanide and cyanate, just as chlorine forms a mixture of potassium chloride and hypochlorite (comp. p. 105).

Hydrocyanic Acid, or *Prussic Acid*, HCN.—Hydrocyanic acid is formed by the direct union of nitrogen and acetylene when a series of electric sparks is passed through a mixture of these gases:

$$N_2 + C_2H_2 = 2HCN.$$

and also by the action of the silent electric discharge on a mixture of cyanogen gas and hydrogen:

$$C_2N_2 + H_2 = 2HCN.$$

The ordinary mode of preparation and chief properties of this substance have already been mentioned. This acid easily undergoes decomposition, and cannot therefore be kept for a length of time either in the pure state or in aqueous solution. It yields in the latter case ammonium formate, thus:

$$HCN + 2H_2O = HCO.ONH_4;$$

as aceto-nitrile yields acetic acid (Lesson XXXIII.), and hydrocyanic acid is therefore the nitrile of formic acid. With chlorine and bromine it yields cyanogen chloride and bromide. The best method of detecting hydrocyanic acid is founded on the formation of Prussian blue. To the liquid containing the acid a few drops of a ferrous and a ferric salt are added, then excess of caustic soda, and lastly, an excess of hydrochloric acid: the formation of a deep blue liquid, from which a deep blue precipitate separates either at once or after a little time, indicates the presence of hydrocyanic acid. The presence of this substance may also be recognised by evaporating some of the solution on a watch-glass with ammonium sulphide to dryness on a water-bath; on adding a drop of ferric chloride, a deep red coloration of ferric thiocyanate is produced, if hydrocyanic acid be present.

The simple metallic cyanides are formed by the direct action of hydrocyanic acid upon a metallic oxide: in addition to these a large number of *double cyanides* is known.

Potassium Cyanide, KCN. is formed when potassium is burnt in cyanogen or in hydrocyanic acid gas, or when potash is added to aqueous hydrocyanic acid. It is prepared on a large scale by fusing potassium ferrocyanide either alone or with potassium carbonate. The iron is in the latter case separated, and potassium takes its place. Potassium cyanide is a white salt, very soluble in water and hot alcohol; it fuses easily without decomposition, and acts as a violent poison. Potassium cyanide is used in photography for dissolving the unaltered silver salts, forming a soluble double salt, $KCN + AgCN$; also in still greater quantity in the art of electrotyping in gold and silver, serving as a solvent for these metals, the above double salt and the corresponding gold compound being formed. The sodium and ammonium cyanides are also soluble, very poisonous salts.

Mercuric Cyanide, $Hg.(CN)_2$, is a soluble, easily crystallisable salt, formed by dissolving mercuric oxide in aqueous hydrocyanic acid. When heated it decomposes into gaseous cyanogen $(CN)_2$, mercury, and a brown substance polymeric with cyanogen gas, and called *Paracyanogen.*

The other simple cyanides are insoluble in water; amongst the most important are the white silver cyanide, and the brownish-red copper cyanide. In writing the formulæ of these compounds, it is frequently useful to express cyanogen by the symbol Cy.

Compound Cyanides.

Amongst the numerous compound cyanides, those of potassium and iron are the most important: in these the cyanogen residues are contained in combination in a different mode to that in the ordinary cyanides, viz. in the form of tricyanogen C_3N_3, instead of cyanogen CN. Further, it is to be noted that the union of the cyanogen or tricyanogen groups to metals very frequently alters many of the ordinary tests and reactions of those metals; thus from the compound cyanides of potassium and iron, the latter metal is not precipitated by ammonia or by ammonium sulphide. Similar compounds are formed by cobalt and a few other metals. These bodies may be represented as containing a metallo-organic radical, since the cyanogen groups are very intimately united with the metallic residue, and can only be separated by the use of powerful reagents.

Potassium Ferrocyanide, $K_8Fe_2(C_3N_3)_4 + 6H_2O$.—This salt, commonly called *yellow prussiate of potash*, is made on a large scale by heating nitrogenous organic matter with caustic potash, and adding freshly precipitated ferrous carbonate to the solution of potassium cyanide thus obtained :

$$12KCN + 2FeCO_3 = K_8(C_3N_3)_4Fe_2 + 2K_2CO_3.$$

On evaporating the solution, large yellow quadratic crystals of potassium ferrocyanide, containing six molecules of water of crystallization, are deposited. It acts as a mild purgative and is not poisonous. When heated strongly, it yields potassium cyanide and iron carbide, and when treated with dilute sulphuric acid, hydrocyanic acid is formed. By the action of strong and hot sulphuric acid, the salt is decomposed, and carbonic oxide gas evolved ; thus :

$$K_8Fe_2(C_3N_3)_4 + 12H_2O + 12H_2SO_4 =$$
$$12CO + 2FeSO_4 + 4K_2SO_4 + 6(NH_4)_2SO_4.$$

Ferrous salts produce with solutions of this salt a white precipitate which quickly becomes blue on exposure to air. Ferric salts produce a deep blue precipitate of *Soluble Prussian Blue*, $Fe_4K_2(C_3N_3)_4$; this substance is insoluble in saline solutions, but dissolves in pure water with a deep blue colour. In this liquid an aqueous solution of a ferrous salt produces a deep blue precipitate of *Insoluble Prussian Blue*, $Fe_{10}(C_3N_3)_8$. This valuable pigment is manufactured on the large scale by precipitating yellow prussiate of potash with ferrous sulphate (green vitriol) which has been exposed to the air, and then washing the precipitate with chlorine water. Potassium ferrocyanide gives with solutions of copper salts a chocolate-coloured precipitate of copper ferrocyanide, $Cu_4Fe_2Cy_{12}$.

Hydrogen Ferrocyanide, or *Ferrocyanic Acid*, $H_8Fe_2(C_3N_3)_4$—This acid is formed by adding hydrochloric acid to a strong solution of potassium ferrocyanide ; it separates as a white crystalline powder. It acts as a strong acid, and is octobasic, forming a series of salts in which the eight atoms of hydrogen of the acid are replaced by an equivalent amount of metal.

Potassium Ferricyanide, $K_6Fe_2(C_3N_3)_4$.—This salt, also called *red prussiate of potash*, is obtained by passing chlorine gas through a solution of the yellow prussiate, which thus loses two atoms of potassium. The action must be allowed to continue until a drop of solution produces no blue precipitate with a ferric salt. On evaporation, the salt separates out in deep red prismatic crystals.

By acting with potassium amalgam on an aqueous solution of the ferricyanide it is converted into ferrocyanide. With ferric salts the ferricyanide gives only a brown coloration; with ferrous salts a deep blue precipitate of soluble *Prussian Blue*, $Fe_4K_2(C_3N_3)_4$, is formed.

When insoluble Prussian blue is acted upon by oxidizing agents, it yields another blue, called *Williamson's Blue*, thus :

$$3Fe_{10}(C_3N_3)_8 + 3O = 2Fe_{14}(C_3N_3)_{36} + Fe_2O_3.$$

This compound is also produced when soluble Prussian blue is precipitated by a ferric salt.

Hydrogen Ferricyanide, or *Ferricyanic Acid*, $H_6Fe_2(C_3N_3)_4$, forms reddish brown deliquescent needles.

Nitro-Ferricyanides or *Nitroprussides* are a peculiar class of salts, obtained by the action of nitric acid on potassium ferrocyanide. The *sodium* salt $Na_4Fe_2(C_3N_3)_2(C_2N_2NO)_2$, crystallizes in red prisms, and produces a deep purple colour with the slightest trace of an alkaline sulphide.

Cyanogen Chlorides.

Cyanogen forms with chlorine a chloride which exists in two polymeric modifications; they are both obtained by the action of chlorine upon hydrocyanic acid :

	Boiling Point.		Melting Point.
Liquid Cyanogen Chloride, $CN\,Cl$	12°·6	+	−7°
Solid ,, ,, $C_3N_3Cl_3$	190°	+	+140°

Cyanic Acid and the Cyanates.

Cyanic Acid, CN.OH.—The salts of this acid, termed *cyanates*, are readily formed by the direct oxidation of cyanides, and, together with cyanides, by the action of the cyanogen gas upon alkalis. Cyanic acid itself cannot be prepared in the free state from its salts, as on liberation it at once changes into polymeric modifications called *cyanuric acid* and *cyamelide*, or decomposes by combination with water into carbon dioxide, ammonium salts, and urea. It can, however, be obtained by heating cyanuric acid in a retort, and collecting the volatile cyanic acid in a freezing mixture ; it then forms a colourless mobile liquid, but immediately changes into solid cyamelide when taken out of the freezing mixture. Cyanic acid is a monobasic acid, and in aqueous solution combines with water to form ammonium carbonate,

$$CN.OH + 2H_2O = NH_4HCO_3.$$

Ammonium Cyanate, $CN.ONH_4$, is formed by bringing together dry ammonia and cyanic acid. This salt undergoes gradually at ordinary temperatures, and at once at 100°, a remarkable molecular change, being transformed into ***urea***,

$$CN.OH + NH_3 = CO(NH_2)_2.$$

Cyanuric Acid, $(C_3N_3)(OH)_3$.—This polymer of cyanic acid is a solid crystalline substance formed on heating urea, or by acting with water on the solid cyanogen chloride.

Cyamelide is another solid polymeride of cyanic acid of unknown molecular weight.

Thiocyanic Acid, CN.SH.—The potassium salt of this acid, formerly known as ***sulphocyanide of potassium***, is prepared by heating potassium ferrocyanide with sulphur and potash ; on dissolving and crystallizing, potassium thiocyanate, KSCN, is deposited. The acid may be obtained by acting on mercuric thiocyanate, with sulphuretted hydrogen.

By the action of dilute sulphuric acid on the potassium salt *Carbonyl sulphide*, COS, is produced :

$$CNSH + H_2O = COS + NH_3.$$

(Compare the corresponding reaction shown by the cyanates mentioned above.)

When a soluble thiocyanate is brought into contact with a ferric salt, a deep blood-red coloration of ferric thiocyanate is formed. The *mercuric* salt, $(CNS)_2Hg$, is a white insoluble powder, which burns when heated, swelling up to a large mass, and serves for the preparation of the so-called Pharaoh's serpents.

Cyanamide, $H_2N.CN$ or $C(NH)_2$, is obtained by the action of ammonia on cyanogen chloride, or by the action of mercuric oxide on thio-urea

$$CS(NH_2)_2 + HgO = CN_2H_2 + HgS + H_2O.$$

Several other amido-compounds of cyanogen exist, for the description of which the larger manuals must be consult

CARBONYL AND THIO-CARBONYL COMPOUNDS.

The radical carbonyl, CO, is a dyad, and known in the free state as carbon monoxide or carbonic oxide gas; from it the following compounds are derived :—

Carbonyl chloride, $CO:Cl_2$. Carbonyl oxide or carbon dioxide, $CO:O$. Carbonyl sulphide, $CO:S$. Potassium carbonate, $CO(OK)_2$. Urea, or Carbamide, $CO(NH_2)_2$.

In the thio-carbonyl compounds the existence of the dyad radical thio-carbonyl, CS, is assumed, although it is not known in the free state. Many of the carbonyl compounds are mentioned under carbon in the inorganic portion of this work. The carbonyl compounds, though considered by themselves for the sake of convenience, are like all other organic compounds to be regarded as derivatives of a corresponding hydrocarbon, viz.: marsh gas or methane, CH_4, already referred to. From marsh gas we pass through methyl alcohol $CH_3.OH$, to formic acid $HCO.OH$, and thence to hydroxy-formic acid (compare the hydroxy-fatty acids or lactic acids, which is the hypothetical carbonic acid $HO.CO.OH$. Carbonyl chloride is then the chloride of carbonic acid; urea is the amide of carbonic acid, &c.

The properties of carbonyl or carbonic oxide, CO, have already been described (p. 86). It behaves as an unsaturated compound, and unites directly with chlorine, &c. It also combines, as already mentioned (p. 247), with certain metals, viz. nickel and iron. Two compounds with the latter metal, one liquid, and the other solid, have quite recently been obtained. They have the composition $Fe(CO)_5$ and $Fe_2(CO)_7$.

Carbonyl Chloride, or *Phosgene*, COCl_2, is formed when dry carbon monoxide and dry chlorine gases are brought together in sunlight. At the ordinary temperature it is a colourless gas, but when cooled it condenses to a colourless liquid, boiling at + 8° and possessing an unpleasant, suffocating smell. In contact with water it quickly decomposes into carbon dioxide and hydrochloric acid:

$$\text{COCl}_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{HCl}.$$

Carbonyl Sulphide, COS, is formed by passing carbonic oxide gas and the vapour of sulphur together through a heated porcelain tube, or better, by acting on potassium thiocyanate with dilute sulphuric acid. It is a colourless gas, which burns with a blue flame, and has a peculiar smell somewhat resembling that of sulphuretted hydrogen. It is absorbed by caustic potash with formation of potassium sulphide and carbonate.

Carbamic Acid, $\text{CO}\left\{\begin{matrix}\text{NH}_2\\ \text{OH}\end{matrix}\right.$, is not known in the free state, but the ammonium salt is formed when dry carbon dioxide and dry ammonia gas are brought together, and is a constituent of ordinary ammonium carbonate or *sal volatile;* with water it forms ammonium carbonate:

$$\text{CO}\left\{\begin{matrix}\text{NH}_2\\ \text{O.NH}_4\end{matrix}\right. + \text{H}_2\text{O} = \text{CO}\left\{\begin{matrix}\text{O.NH}_4\\ \text{O.NH}_4.\end{matrix}\right.$$

Urea, or *Carbamide*, $\text{CO}\left\{\begin{matrix}\text{NH}_2\\ \text{NH}_2\end{matrix}\right.$.—This important substance is found in large quantity in the urine of mammalia, and in small amount in various animal juices. It is obtained artificially—(1) From ammonium cyanate (see p. 305):

$$\text{CN.ONH}_4 = \text{CO(NH}_2)_2.$$

(2) By the action of ammonia on carbonyl chloride, thus:

$$\text{COCl}_2 + 4\text{NH}_3 = \text{CO(NH}_2)_2 + 2\text{NH}_4\text{Cl}.$$

The first of these methods is that by which urea is best prepared. For this purpose yellow prussiate of potash is mixed with manganese dioxide, and the mixture heated on an iron plate; potassium cyanate is thus formed, and this salt is dissolved in water and mixed with ammonium sulphate. On evaporating to dryness urea is formed, and this can be extracted from the residue with alcohol. This reaction, which was discovered by Wöhler in 1828, is of great historical interest, inasmuch as it was the first recognized instance of the synthesis from its elements of any product of animal or vegetable life. Urea thus prepared crystallizes in long striated needles, which dissolve in their own weight of cold water, and to the same extent in hot alcohol. When heated to 120°, urea fuses and begins to decompose, forming substances termed *ammeline* and *biuret;* whilst at a higher temperature cyanuric acid is produced. When heated with water in closed tubes to 100°, urea forms carbonic acid and ammonia, *i.e.* ammonium carbonate, showing that it is an amide of carbonic acid. Nitrous acid decomposes urea instantly into carbonic acid, nitrogen, and water:—

$$CO(NH_2)_2 + 2HNO_2 = CO_2 + 3H_2O + 2N_2.$$

Urea is the product of the oxidation of the nitrogenous constituents of the body, and the quantity of urea excreted is a measure of the activity of the changes going on. Urea forms compounds with acids and with bases. *Urea nitrate* $CO(NH_2)_2NO_3H$, and *oxalate*, $2\ (CO(NH_2)_2)C_2O_4H_2$, are the most important salts. With mercuric oxide urea forms an important insoluble compound, $Hg(NO_3)_2 + 2\ CO(NH_2)_2 + 3HgO$, which is employed as a means of estimating the quantity of urea in a solution.

Thiocarbonic Acid, $CS(SH)_2$.—Just as carbon dioxide unites with metallic oxides to form carbonates, so carbon disulphide unites with metallic sulphides to form thiocarbonates. Thus sodium thiocarbonate is formed by dissolving carbon disulphide in a solution of sodium sulphide. On addition of hydrochloric acid to an alkaline thio-carbonate, thiocarbonic acid separates out as a heavy, brown, peculiarly smelling oil.

Thiocarbamide, or *Thio-Urea*, $CS(NH_2)_2$, is formed by heating ammonium thiocyanate to 140°. It crystallizes in long colourless needles and, like urea, combines with acids to form salts.

LESSON XXXI

PARAFFIN GROUP

Hydrocarbons of the Series C_nH_{2n+2}.—The hydrocarbons of the series of which marsh gas CH_4 is the first term, are distinguished by being unattacked by such powerful oxidizing agents as nitric and chloric acids. Hence they have been termed paraffins (from *parum affinis*). Chlorine when brought into contact with them gives rise to substitution-products; at first one atom of hydrogen is replaced, giving rise to the chlorides of the monad radicals, whilst on further action more than one atom is similarly replaced. Thus, marsh gas first yields methyl chloride.

$$CH_4 + Cl_2 = CH_3Cl + HCl,$$

and afterwards higher chlorinated products are formed.

Paraffins can be obtained in several ways:

1. By bringing the iodide of an alcohol radical in contact with zinc and hydrochloric acid:

$$CH_3I + H_2 = CH_4 + HI.$$

2. By heating these iodides in closed vessels together with zinc, when zinc iodide is formed and the radicals liberated. These however are incapable of existence in the free state and combine together.

$$2CH_3I + Zn = 2CH_3 + ZnI_2$$
$$CH_3 + CH_3 = C_2H_6.$$

The paraffins are also formed in the dry distillation of many organic bodies, and are contained in coal- and wood-tar, as well as in the several kinds of *rock-oil*, or *petroleum*, some of which, such as those of Pennsylvania, consist almost wholly of these hydrocarbons.

The following list contains the name, composition, and boiling-point of the best investigated of the paraffins:

		B.P.
Methane	CH_4	Gaseous.
Ethane	C_2H_6	,,
Propane	C_3H_8	,,
Butane	C_4H_{10}	1°
Pentane	C_5H_{12}	38°
Hexane	C_6H_{14}	70°
Heptane	C_7H_{16}	99°
Octane	C_8H_{18}	124°
Dodecane	$C_{12}H_{26}$	202°
Hecdecane	$C_{16}H_{34}$	278°

In these ten compounds, termed the *normal paraffins*, the carbon atoms are connected together in a single chain; thus, the constitution of pentane is the following:

$$CH_3—CH_2—CH_2—CH_2—CH_3.$$

It has already been stated (p. 285) that several isomeric modifications of these hydrocarbons exist, so that we now know of two butanes and three pentanes which are described in greater detail below. The paraffins are largely used in the arts and manufactures; thus, the lighter and more volatile portions of petroleum are used as solvents for gums, fats, resins, &c.; the less volatile portions are employed for illuminating purposes, whilst the still less volatile parts form a useful grease for lubrication, and for medicinal use, as *vaseline*, and the highest portions yield the beautiful white solid *paraffin wax*, now much employed for making candles.

COMPOUNDS OF MONAD RADICALS.

General Characteristic of Monad Alcohols.—The monovalent alcohols and their derivatives form a very large and important group of organic compounds. As an example of these alcohols we may take ethyl alcohol, C_2H_6O, known as *spirits of wine:* this substance, in common with all the other alcohols of this series, may be considered as water in which one atom of hydrogen is replaced by a radical, having in this case the formula C_2H_5; hence ethyl alcohol is $C_2H_5.OH$. Ethyl alcohol is in constitution analogous to caustic potash, KOH; and as, by adding hydrochloric acid to the later, we get KCl (potassium chloride) and H_2O; so the chlorides, iodides, and bromides of all the alcohol radicals can be obtained by treating the alcohol with the hydracid under certain conditions. The analogy of the ethyl with the potassium compounds is still further seen in the fact that an ethyl compound exists which stands to alcohol in the same relation as potassium monoxide, $\left.\begin{matrix}K\\K\end{matrix}\right\}O$, to caustic potash; this compound is common or ethyl ether, $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$. We also know analogous compounds to the potassium salts; thus we have:

Potassium chloride, KCl.	Ethyl chloride, $C_2H_5.Cl$.
Potassium nitrate, $KO.NO_2$.	Ethyl nitrate, $C_2H_5O.NO_2$.
Hydrogen potassium sulphate, $KO.SO_2.OH$.	Hydrogen ethyl sulphate, $C_2H_5O.SO_2.OH$.
Potassium sulphate, $KO.SO_2.OK$.	Ethyl sulphate, $C_2H_5O.SO_2.OC_2H_5$.
Potassium acetate, $KO.C_2H_3O$.	Ethyl acetate, $C_2H_5O.C_2H_3O$.

Compound Ammonias and Organo-metallic bodies.—Each alcoholic radical also forms a series of compound ammonias, or amines; that is, ammonia, $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, in which one or more atoms of hydrogen are replaced by a radical: thus, for the ethyl series we have ethylamine, $\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$ or $C_2H_5.NH_2$; diethylamine, $\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}N$ or $(C_2H_5)_2NH$; and triethylamine, $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}N$ or $(C_2H_5)_3N$. To the first class, in which one of hydrogen is replaced by an organic radical, the name of *primary amines* is given. To the second, having two atoms replaced, that of *secondary amines*, whilst to the third class the term *tertiary amines* is applied. We can, indeed, go one step further in the addition of ethyl, and obtain a caustic substance resembling potash in its properties, and analogous to the ammonium hydroxide, $NH_4.OH$, but containing 4 of ethyl in place of the 4 of hydrogen; thus $N(C_2H_5)_4.OH$: to this substance the name of tetra-ethyl-ammonium hydroxide is given.

Compounds of the alcohol radicals analogous to arsenic and phosphorus trihydrides are also known: thus for instance, $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\}$ As or $(CH_3)_3As$, trimethylarsine, and $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}P$ or $(C_2H_5)_3P$, triethylphosphine, are known. The alcohol radicals likewise combine with metals, such as zinc, tin, &c., to form bodies which in their turn combine with chlorine, &c., and have, therefore, been termed the ***organo-metallic bodies:*** such substances are zinc ethyl and tin tetra-ethyl. These may be considered as the corresponding chlorides in which the chlorine has been replaced by the organic radical; thus:

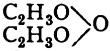
$$\text{Zinc chloride, } Zn\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.; \qquad \text{Zinc ethyl, } Zn\left\{\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right.;$$

$$\text{Stannic chloride, } Sn\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\end{matrix}\right.; \quad \text{Tin tetra-ethyl, } Sn\left\{\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\\C_2H_5.\end{matrix}\right.$$

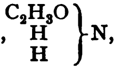
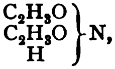
Fatty Acids and Aldehydes.—When ethyl alcohol is exposed to the action of oxidizing agents it loses two atoms of hydrogen, and is converted into the compound C_2H_4O, known as *acetic aldehyde;* this can, from its composition, no longer contain the radical C_2H_5 which must itself have undergone alteration in the process of oxidation. It will be shown later that aldehyde also no longer contains the hydroxyl group; if, however, it be further treated with oxidizing agents it takes up another atom of oxygen forming *acetic acid* $C_2H_4O_2$, which is found to contain the hydroxyl group, and may therefore be represented as $C_2H_3O.OH$, whilst aldehyde may be represented as the hydride of the same radical (which is known as *acetyl*) thus $C_2H_3O.H$. Aldehyde readily takes up two atoms of hydrogen on reduction reforming alcohol, but acetic acid cannot, on the other hand, be directly reduced to aldehyde.

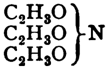
Every alcohol which, like ethyl alcohol, $CH_3.CH_2.OH$ contains the group $CH_2.OH$ is converted on oxidation first into the aldehyde and then into the corresponding acid. The latter series differ from the corresponding alcohols inasmuch as they contain an atom of oxygen in place of two atoms of hydrogen.

Ethyl alcohol, $C_2H_5.OH$	Acetic acid, $C_2H_3O.OH$
Butyl alcohol, $C_4H_9.OH$.	Butyric acid, $C_4H_7O.OH$.

All these acids are monobasic. *i.e.* they contain one atom of hydrogen replaceable by a metal; this may also be replaced by an alcohol radical such as ethyl, which yields *ethyl acetate* or *acetic ether* $C_2H_3O.OC_2H_5$, and also by radicals like acetyl itself, which gives *acetic anhydride*  $\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!\!>O$, a substance which may also be termed *acetyl oxide*. Further, the hydroxyl group in acetic acid may be replaced by halogens, with formation of such compounds as *acetyl chloride* $C_2H_3O.Cl$.

The acid-radicals can also replace one or more of the hydrogen atoms in ammonia, giving rise to a class of compound ammonias termed *amides*: thus we have with acetyl:

Acetamide,  $\left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N$, or $C_2H_3O.NH_2$; diacetamide,  $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right\}N$, or $(C_2H_3O)_2NH$.

and triacetamide,  $\left.\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_3O\end{matrix}\right\}N$, or $(C_2H_3O)_3N$.

The fatty acids in many reactions undergo a change in which one atom of carbon is eliminated as carbon dioxide. Thus when a galvanic current is passed through a solution of potassium acetate, it is converted into carbon dioxide, hydrogen and ethane, the latter being formed by the union of the methyl groups first set free:

$$2C_2H_3O.OH = 2CO_2 + H_2 + CH_3—CH_3.$$

Also, as already mentioned, when an acetate is heated with an alkali it yields methane and a carbonate:

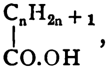
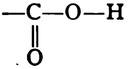
$$C_2H_3O.ONa + NaOH = CH_4 + Na_2CO_3.$$

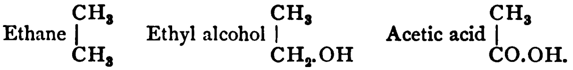
On the other hand fatty acids may be obtained from compounds of the alcohol radicals containing one less atom of carbon than the acid itself. Thus methyl forms a compound with sodium CH_3Na, which unites directly with carbon dioxide forming sodium acetate.

$$CH_3.Na + CO_2 = CH_3.CO_2Na.$$

If the iodine in methyl iodide be replaced by cyanogen we obtain *methyl cyanide* or *acetonitrile*, which on treatment with caustic potash yields ammonia and potassium acetate:

$$CH_3.CN + KOH + H_2O = C_2H_3O.OK + NH_3.$$

These reactions show that acetic acid must contain the methyl group; the formula given above, $C_2H_3O.OH$ does not show this, but simply implies that the substance contains the hydroxyl group and the radical C_2H_3O, which remains unaltered in a number of reactions. To account however for the above decompositions and syntheses of acetic acid, we must resolve the group C_2H_3O further into $CH_3.CO$, acetic acid then becoming $\begin{array}{l} CH_3 \\ | \\ CO.OH \end{array}$. The other acids of this series may therefore be represented by the general formula  $\begin{array}{l} C_nH_{2n+1} \\ | \\ CO.OH \end{array}$, and they may therefore be regarded as compounds of the alcohol radicals with the monad group —CO.OH or  $\begin{array}{l} —C—O—H \\ \| \\ O \end{array}$, in which one of the carbon valencies is saturated by the hydroxyl group, two others by an oxygen atom, whilst the fourth combines with the alcohol radical. This group is found in by far the larger number of organic acids and is known as *Carboxyl.* The relations between ethane, ethyl alcohol, and acetic acid are represented therefore as follows

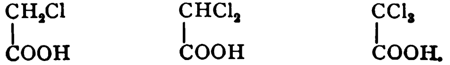


$$\text{Ethane} \begin{array}{l} CH_3 \\ | \\ CH_3 \end{array} \qquad \text{Ethyl alcohol} \begin{array}{l} CH_3 \\ | \\ CH_2.OH \end{array} \qquad \text{Acetic acid} \begin{array}{l} CH_3 \\ | \\ CO.OH. \end{array}$$

The carboxyl group is formed by the oxidation of a methyl group, it is also, as we have already seen, formed by the action of alkalis on the cyanogen group CN.

The hydrogen in the alcohol radicals of the fatty acids may be replaced by halogens, without any great alteration taking place in the properties of the compounds. Thus we know three chlorinated acetic acids:

Chloracetic acid. Dichloracetic acid. Trichloracetic acid.



$$\begin{array}{l} CH_2Cl \\ | \\ COOH \end{array} \qquad \begin{array}{l} CHCl_2 \\ | \\ COOH \end{array} \qquad \begin{array}{l} CCl_3 \\ | \\ COOH. \end{array}$$

In the same manner the oxygen atom of the hydroxyl group may be replaced by sulphur, and we then get

Hydrogen thiacetate.	Potassium thiacetate.	Ethyl thiacetate.
$CH_3.CO.SH$	$CH_3.CO.SK$	$CH_3.CO.SC_2H_5$.

The following is a list of the better-known primary alcohols and fatty acids, giving their formulæ, and boiling and melting points :—

Primary Normal Alcohols and corresponding Normal Fatty Acids.					
		B.P.			B.P.
Methyl Alcohol .	CH_4O	66°.	Formic Acid .	CH_2O_2	100°.
Ethyl ,, .	C_2H_6O	78°.4.	Acetic ,, .	$C_2H_4O_2$	118°.
Propyl ,, .	C_3H_8O	97°.	Propionic ,, .	$C_3H_6O_2$	141°.
Butyl ,, .	$C_4H_{10}O$	116°.	Butyric ,, .	$C_4H_8O_2$	163°.
Pentyl ,, .	$C_5H_{12}O$	137°.	Pentylic ,, .	$C_5H_{10}O_2$	185°.
Hexyl ,, .	$C_6H_{14}O$	157°.	Hexylic ,, .	$C_6H_{12}O_2$	205°.
Heptyl ,, .	$C_7H_{16}O$	176°.	Heptylic ,, .	$C_7H_{14}O_2$	224°.
Octyl ,, .	$C_8H_{18}O$	195°.	Octylic ,, .	$C_8H_{16}O_2$	236°.
			Nonylic ,, .	$C_9H_{18}O_2$	254°.
Continuation of Higher Normal Fatty Acids.					
		M.P.			M.P.
Capric Acid .	$C_{10}H_{20}O_2$	30°.	Stearic Acid .	$C_{18}H_{36}O_2$	69°.2.
Lauric ,, .	$C_{12}H_{24}O_2$	43°.	Arachidic ,, .	$C_{20}H_{40}O_2$	75°.
Myristic ,, .	$C_{14}H_{28}O_2$	53°.8.	Behenic ,, .	$C_{22}H_{44}O_2$	73°.
Palmitic ,, .	$C_{16}H_{32}O_2$	62°.	Cerotic ,, .	$C_{27}H_{54}O_2$	78°.
Margaric ,, .	$C_{17}H_{34}O_2$	59°.9.	Melissic ,, .	$C_{30}H_{60}O_2$	90°.
Primary[1] Iso-alcohols and corresponding Iso-Fatty Acids.					
		B.P.			B.P.
Isobutyl Alcohol .	$C_4H_{10}O$	109°.	Isobutyric Acid .	$C_4H_8O_2$	153°.
Amyl ,, .	$C_5H_{12}O$	132°.	Valerianic ,, .	$C_5H_{10}O_2$	175°.
Isohexyl ,, .	$C_6H_{14}O$	150°.	Isohexylic ,, .	$C_6H_{12}O_2$	199°.
Isoheptyl ,, .	$C_7H_{16}O$	165°.	Isoheptylic ,, .	$C_7H_{14}O_2$	212°.

Primary, Secondary, and Tertiary Alcohols.—The monad alcohols are divided into three groups, viz., the primary, secondary, and tertiary alcohols.

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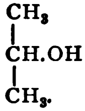
[1] The primary iso-alcohols are related to the primary normal alcohols in the same way as the iso-paraffins are related to the normal paraffins (see p. 310.)

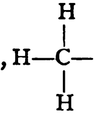
1. *Primary Alcohols.*—This class is characterised from the two following by the fact that on oxidation the alcohols yield *aldehydes* and *acids* containing the same number of carbon atoms. They all contain the group $—CH_2OH$, which as it is monatomic can only occur at the end of the chain, as shown in the formula of ethyl alcohol $CH_3.CH_2OH$

2. *Secondary Alcohols.*—In this class of alcohols, the hydroxyl group is attached to a carbon atom which is also combined with two other carbon atoms. A glance at the figures on p. 277, shows that this is first possible in the 3 carbon or propyl series. The primary and secondary alcohols containing the same number of carbon atoms are isomeric (p. 284) but differ in many of their properties and in the decompositions which they undergo.

Secondary propyl alcohol is represented by the formula

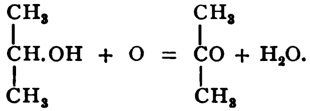


$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_3.\end{array}$$

and is also known as *dimethylcarbinol*, as it may be regarded as formed from methyl alcohol,  $\begin{array}{c}\quad H\\ \quad |\\ H—C—O—H\\ \quad |\\ \quad H\end{array}$ (which is also termed carbinol) by replacing two atoms of hydrogen by methyl.

On oxidation the secondary alcohols like the primary compounds lose two atoms of hydrogen; the compounds formed differ however in many respects from the aldehydes and are known as ketones. Thus:

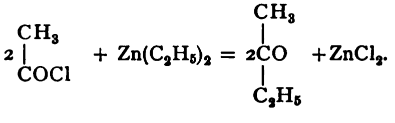
Dimethyl carbinol. Dimethyl ketone or acetone.



$$\begin{array}{l}CH_3\\ |\\ CH.OH\\ |\\ CH_3\end{array} + O = \begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} + H_2O.$$

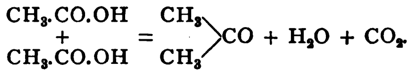
The ketones take up hydrogen, forming the secondary alcohols; on oxidation they do not yield the corresponding acid, but split up into acids containing a smaller number of carbon atoms.

Every ketone contains two alcohol-radicals, united by the group CO. They are formed by several other reactions; thus, if zinc ethyl is acted upon by acetyl chloride methylethylketone is obtained:



$$2\begin{array}{c}CH_3\\|\\COCl\end{array} + Zn(C_2H_5)_2 = 2\begin{array}{c}CH_3\\|\\CO\\|\\C_2H_5\end{array} + ZnCl_2.$$

Ketones are also produced when the salts of the fatty acids are subjected to dry distillation, or when the vapour of the acid is passed through a red-hot tube. Thus acetic acid yields acetone:



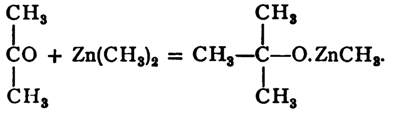
$$\begin{array}{c}CH_3.CO.OH\\+\\CH_3.CO.OH\end{array} = \begin{array}{c}CH_3\\CH_3\end{array}\!\!>CO + H_2O + CO_2.$$

3. *Tertiary Alcohols.*—In the third class of alcohols the hydroxyl (OH) is attached to a carbon atom which is connected with three other carbon atoms. These alcohols do not yield any corresponding aldehydes, acids, or ketones, but on oxidation at once split up into acids or ketones containing a lower number of carbon atoms.

The first term of this class is that of the four-carbon series, tertiary butyl alcohol, or trimethylcarbinol, and is obtained by the action first of zinc methyl on acetyl chloride, and afterwards by that of water on the product:

(1) $CH_3.CO.Cl + Zn(CH_3)_2 = CH_3.CO.CH_3 + ZnCl(CH_3)$.

(2)



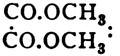
$$\begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} + Zn(CH_3)_2 = CH_3-\begin{array}{c}CH_3\\|\\C\\|\\CH_3\end{array}-O.ZnCH_3.$$

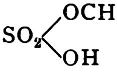
(3) $(CH_3)_3C.OZnCH_3 + H_2O = (CH_3)_3C.OH + ZnO + CH_4$.

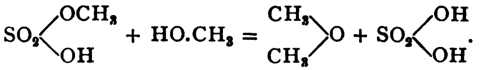
A delicate test for distinguishing between primary, secondary, and tertiary alcohols and their derivatives is described later on.

MONOCARBON OR METHYL SERIES.

Methyl Alcohol, $CH_3.OH$, commonly called Wood-spirit, is produced in the dry distillation of wood, forming about one per cent. of the aqueous distillate: it is likewise met with in the oil of winter-green, derived from the *Gaultheria Procumbens*. Methyl alcohol can likewise be synthetically built up from its constituent elements by means of several reactions, which will afterwards be mentioned.

Pure methyl alcohol is obtained from crude wood-spirit, in which it is contained mixed with a variety of other organic compounds, first by fractional distillation, and then by forming from the crude methyl alcohol so obtained a crystalline methyl oxalate,  $\begin{array}{l}CO.OCH_3\\ \dot{C}O.OCH_3\end{array}$: this, on distillation with water, is decomposed, and yields the alcohol in the pure but dilute state. From the accompanying water it is freed by means of quicklime. Methyl alcohol is a colourless, mobile liquid, possessing a pure spirituous smell; the specific gravity of the liquid is 0·8142 at 0°, and its boiling-point is 66°. It burns with a non-luminous flame, and is soluble in, and miscible with, water. Potassium dissolves in methyl alcohol with evolution of hydrogen and formation of potassium methylate, $CH_3.OK$. Methyl alcohol when acted on by oxidizing agents yields methyl aldehyde and formic acid; acted upon by hydrochloric acid, in presence of a dehydrating agent, the alcohol yields methyl chloride.

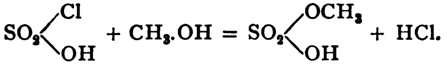
Of especial interest is the action of sulphuric acid on methyl alcohol. The liquids mix with evolution of heat together forming *methylsulphuric acid* or *methyl hydrogen sulphate*,  $SO_2\begin{array}{l}\diagup OCH_3\\ \diagdown OH\end{array}$ and water, H_2O; if the former be heated with another molecule of methyl alcohol the following change occurs:



$$SO_2\begin{array}{l}\diagup OCH_3\\ \diagdown OH\end{array} + HO.CH_3 = \begin{array}{l}CH_3\diagdown\\ CH_3\diagup\end{array}O + SO_2\begin{array}{l}\diagup OH\\ \diagdown OH\end{array}.$$

The *dimethyl ether* thus formed is a colourless gas, which has an ethereal odour and condenses at—21° to a colourless liquid.

Methylsulphuric acid $CH_3.HSO_4$ is also obtained by acting on methyl alcohol with chlorosulphuric acid :



$$SO_2\begin{cases}Cl\\OH\end{cases} + CH_3.OH = SO_2\begin{cases}OCH_3\\OH\end{cases} + HCl.$$

It is an oily liquid, whose aqueous solution readily decomposes into sulphuric acid and methyl alcohol, it is a monobasic acid and forms a series of crystalline salts.

Methane, *Methyl Hydride*, or *Marsh Gas*, CH_4.—As we have seen (p. 88), this gas occurs in nature as fire-damp and the gas of marshes. It can be obtained easily by heating sodium acetate with a caustic alkali, the acetic acid splitting up into carbon dioxide and marsh gas : $CH_3.COOH = CH_4 + CO_2$. Methane can also be obtained by passing the vapour of carbon disulphide, together with sulphuretted hydrogen gas, through a red hot tube ; and in this way it may be built up from its constituent elements. It may likewise be obtained by heating methyl iodide together with zinc and water. Methane is a colourless inflammable gas, which burns with a slightly luminous flame, and when mixed with air produces a dangerously explosive mixture. Most oxidizing agents do not act upon this hydrocarbon, but chlorine attacks it in the presence of sunlight with such violence as to produce an explosion. By the slow action of chlorine, several *substitution products* are formed, the chief of which are methyl chloride, CH_3Cl, chloroform, $CHCl_3$, and carbon tetrachloride, CCl_4.

Methyl Chloride, CH_3Cl, is obtained as a colourless gas, condensing at – 21°, by acting upon methyl alcohol with phosphorus pentachloride or with hydrochloric acid in presence of zinc chloride : it is also formed along with other substances by the action of chlorine upon marsh gas. When heated with potash in sealed tubes to 100° potassium chloride and methyl alcohol are formed :

$$CH_3Cl + KHO = CH_3.OH + KCl.$$

The *bromide* and *iodide* are colourless liquids, prepared by acting on methyl alcohol with bromine and iodine in presence of phosphorus.

Chloroform, $CHCl_3$, is formed when chlorine acts on marsh gas, but it is prepared by acting upon ethyl alcohol with bleaching-powder, several secondary reactions taking place; by the action of bleaching-powder on methyl alcohol, no chloroform is obtained. It is a mobile, heavy liquid possessing a powerful and agreeable smell; its specific gravity is 1·525 at 0°, and it boils at 62°. Chloroform is much used in medicine, producing, when it is inhaled, a temporary but perfect insensibility to pain, and is therefore much valued in surgical operations. Many other volatile organic bodies act in a similar manner. Very small quantities of chloroform can be detected by heating the liquid in a test-tube with a few drops of aniline and of an alcoholic solution of caustic soda. If chloroform be present the penetrating and disagreeable odour of phenyl carbamine is noticed. An iodine compound, analogous to chloroform has been prepared; it is termed *Iodoform* CHI_3, is a yellow solid body, and is largely used in surgery.

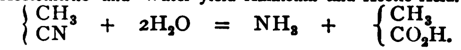
Carbon Tetrachloride, CCl_4, is a colourless liquid, boiling at 77°, obtained as the last product of the action of chlorine on marsh gas. When this substance is brought into contact with sodium amalgam and water, an opposite substitution of hydrogen for chlorine occurs, marsh gas and all the intermediate products being formed.

Methyl Cyanides.—When methyl iodide is heated with silver cyanide, two isomeric compounds of the above composition are formed. They are both colourless liquids; one, which boils at 58°, is characterised by possessing an extremely disagreeable smell. This cyanide, which is called *Methyl Carbamine*, is easily decomposed by acids into formic acid and methylamine:

$$\begin{array}{ccccccc} \text{Methyl Carbamine} & \text{and} & \text{Water} & \text{yield} & \text{Methylamine} & \text{and} & \text{Formic Acid.} \\ CN.CH_3 & + & 2H_2O & = & NH_2CH_3 & + & CH_2O_2. \end{array}$$

From this decomposition we see that the cyanogen group is connected with the methyl by the atom of nitrogen. The other isomeride has been called *Acetonitrile*, and is best prepared by distilling a mixture of potassium cyanide and potassium methyl-sulphate. It boils at 77°, and is not acted upon by acids. In presence of potash it is converted into ammonia and acetic acid:

Acetonitrile and Water yield Ammonia and Acetic Acid.



$$\left\{\begin{array}{l}CH_3\\CN\end{array}\right. + 2H_2O = NH_3 + \left\{\begin{array}{l}CH_3\\CO_2H.\end{array}\right.$$

The constitution of this substance is still more clearly shown by the fact that it combines directly with nascent hydrogen to form ethylamine :

Acetonitrile and Hydrogen yield Ethylamine.

$$CH_3.CN + 2H_2 = CH_3.CH_2NH_2.$$

Hence we see that the two atoms of carbon are combined together, and that this compound really belongs to the ethyl series (see below). The nitriles form a large and also very important class of compounds, as they enable us to pass from one series of compounds (*i.e.* methyl or ethyl, &c.) to the acid of the next higher series (*i.e.* acetic or propionic acids).

LESSON XXXII

DICARBON OR ETHYL SERIES

THE starting-point of this important series is common alcohol or spirits of wine, C_2H_6O ; this is the ethyl hydroxide, and like its numerous and well-known derivatives, contains the radical ethyl C_2H_5.

Ethyl Alcohol, $C_2H_5.OH$, is obtained in the vinous fermentation of sugar, a decomposition effected in aqueous sugar solutions in presence of yeast, in which alcohol and carbonic acid are chiefly formed : the other products of fermentation are described under Cane-Sugar.

Alcohol and alcoholic liquids are prepared in large quantities by the fermentation of sugar derived from various sources. The fermented liquid is distilled, and the dilute aqueous spirit thus separated from non-volatile impurities : it is obtained in a more concentrated form by repeated rectifications, as it boils at a lower temperature than water. Alcohol cannot, however, be completely separated from water by simple distillation, the strongest spirit which can thus be prepared containing 10 per cent. of water. To withdraw all the water, the spirit must be distilled with some substance capable of combining with water, such as potassium carbonate or quicklime. The pure liquid thus obtained is termed *absolute alcohol;* it is a colourless, mobile liquid, possessing a pleasant, spirituous smell and burning taste; its specific gravity at 0° is 0·80625, and at 15°, 0·79367; it boils at 78°·4 when the barometer stands at 760 mm. It has lately been solidified, by exposure to a very low temperature. Alcohol is very inflammable, burning with a slightly luminous blue flame. It absorbs moisture with great avidity, and mixes with water in all proportions, the mixture increasing in temperature and undergoing contraction in volume.

Alcohol can also be prepared from its elements by synthesis. This is done by obtaining acetylene, C_2H_2, by the direct union of carbon and hydrogen (page 89), and combining this directly with hydrogen to form olefiant gas, C_2H_4; this substance combines directly with strong sulphuric acid, forming hydrogen ethyl-sulphate, $C_2H_5.HSO_4$, which, when boiled with water yields sulphuric acid and alcohol by exchange of ethyl for hydrogen:

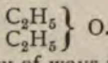
$$C_2H_5.HSO_4 + H_2O = H_2SO_4 + C_2H_5.OH.$$

Olefiant gas also combines with hydriodic acid to form ethyl iodide, which yields alcohol when heated with caustic potash.

Many salts, as well as gases, dissolve in alcohol; it likewise acts as a solvent for resins, organic bases, and essential oils, many of which do not dissolve in water. The determination of the strength of spirit, when free from sugar or other soluble matters, is ascertained by determining the specific gravity by means of delicate hydrometers, and refering to accurate tables, showing the percentage of water. In these estimations the temperature must be accurately observed, and corrections for deviations made, as alcohol expands considerably with increase of temperature, and the specific gravity is thereby altered. The "proof spirit" of the Excise contains 50·8 parts by weight of alcohol to 49·2 of water, and possesses a specific gravity of 0·920 at 15°·5. Weaker spirits are termed *under proof* and stronger spirits *over proof.* Thus 25° over proof means that 100 volumes of this spirit diluted with water yields 125 volumes of proof spirit; whilst 25° under proof means that it contains in 100 volumes seventy-five volumes of proof spirit. Owing to the high duty on pure spirit, the Government allow the sale of a mixture of ninety parts of strong alcohol with ten parts of wood-spirit for manufacturing and scientific purposes; this substance is called "methylated spirit," and is most useful to the scientific and manufacturing chemist. Spirits, wines, and beer contain more or less alcohol, flavoured with certain essential oils, sugar, or extracts. Brandy, whisky, and the other spirits contain from 40 to 50 per cent. of alcohol; wines from 17 (madeira and port) to 7 or 8 (light claret and hock) per cent., whilst strong ale and porter contain from 6 to 8 per cent.

Alcohol is decomposed when its vapour is passed through a red-hot tube; hydrogen, marsh gas, olefiant gas, naphthalene, benzene, and other products being formed. By oxidation alcohol is transformed first into aldehyde and then into acetic acid. This oxidation may be effected by the atmospheric oxygen in presence of finely-divided platinum, or more slowly when certain ferments are present (see Acetic Acid, p. 338). The alkali-metals attack alcohol with rapidity, evolving hydrogen, and forming potassium or sodium ethylate, $C_2H_5.OK$. Hydrochloric acid converts it, though only slowly, into ethyl chloride and water, and the corresponding bromine and iodine compounds act similarly. Strong sulphuric acid combines with alcohol to form hydrogen ethyl-sulphate, or ethylsulphuric acid, a substance which forms salts called the ethyl-sulphates: thus potassium ethyl-sulphate is $C_2H_5.KSO_4$.

The most delicate test for the presence of alcohol depends on the formation of iodoform (p. 320). Drop a crystal of iodine into the liquid to be examined, and then just enough caustic potash to cause the solution to become colourless, when either at once or after a short time a yellow precipitate of iodoform is thrown down.

Ether, or *Diethyl Ether*,  $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O$.—This important substance is formed in a variety of ways from ethyl compounds. The most simple reaction by which ether can be prepared is that of acting upon potassium ethylate with ethyl iodide, an exchange of ethyl and potassium taking place :

Ethyl Iodide and Potassium Ethylate give Potassium Iodide and Ether.

$$C_2H_5I + C_2H_5OK = KI + (C_2H_5)_2O.$$

The reaction by which ether is prepared on the large scale consists in the heating a mixture of alcohol and sulphuric acid to 140°, and passing in fresh quantities of alcohol, when ether and water are given off. The decompositions which here take place are as follows : in the first place, alcohol and sulphuric acid form hydrogen ethyl-sulphate (sulphovinic acid) and water, by an exchange of hydrogen and ethyl :

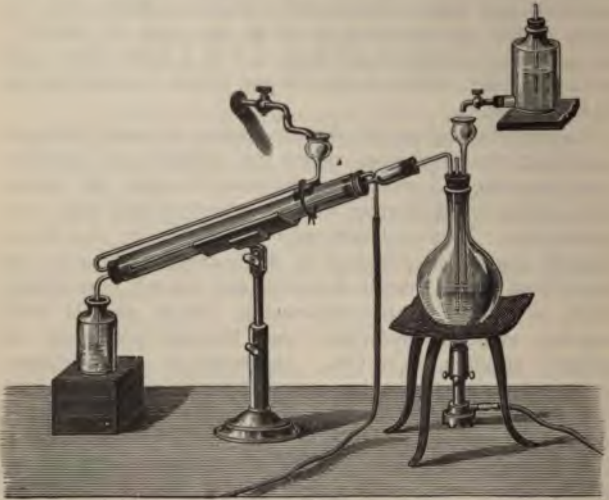
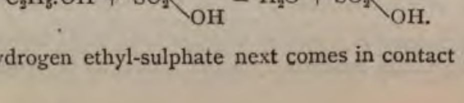


FIG 76.

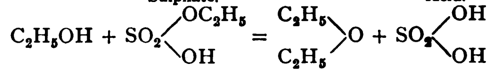
Alcohol and Sulphuric Acid yield Water and Hydrogen Ethyl Sulphate.



$$C_2H_5.OH + SO_2\begin{cases}OH\\OH\end{cases} = H_2O + SO_2\begin{cases}OC_2H_5\\OH.\end{cases}$$

This hydrogen ethyl-sulphate next comes in contact with a second molecule of alcohol, another exchange of hydrogen for ethyl occurs, and ether and sulphuric acid are formed :

Alcohol. Hydrogen-Ethyl Sulphate. Ether. Sulphuric Acid.



$$C_2H_5OH + SO_2\begin{cases}OC_2H_5\\ OH\end{cases} = \begin{matrix}C_2H_5\\ C_2H_5\end{matrix}\Big\rangle O + SO_2\begin{cases}OH\\ OH\end{cases}$$

The water formed by the first decomposition, and the ether produced by the second, are given off as vapour, whilst the sulphuric acid remains behind, ready again to go through the same series of changes on meeting with two other molecules of alcohol. This process is called the *continuous etherification process*, as a current of alcohol may be passed continuously through the sulphuric acid heated to 140°, and a regular supply of ether and water thus obtained. Fig. 76 shows the arrangement of apparatus used for making ether by the above process.

Ether is a colourless, very mobile liquid, possessing a strong and peculiar ethereal smell and solidifies at —129° to a crystaline mass which melts again at —117°·4. It is lighter than water, specific gravity 0·718, and is not miscible with that liquid, though ether is somewhat soluble in water and water slightly in ether. Ether boils at 34°·5, and its vapour is 37 times heavier than hydrogen, and can be poured from vessel to vessel like carbonic acid gas. The vapour burns with a luminous flame, and forms an explosive mixture when mixed with air. From its low boiling point great care must be taken to avoid explosions when working with this substance, owing to the vapour becoming mixed with air. Ether is easily attacked by oxidizing agents, yielding the same products as alcohol; it is also acted upon by chlorine, and a large number of substitution-products formed.

Mixed Ethers containing two different radicals are obtained by acting, for instance, with ethyl iodide upon potassium methylate :

Ethyl Iodide and Potassium Methylate yield Potassium Iodide and Methyl Ethyl Ether.

$$C_2H_5I + CH_3.OK = KI + CH_3.O.C_2H_5.$$

or by acting on hydrogen methyl-sulphate, $CH_3.HSO_4$, with ethyl alcohol. The following is a list of some of the more important simple and mixed ethers of this series :—

Table of Simple and Mixed Ethers.

			Boiling point.
Dimethyl ether	C_2H_6O	$\left.\begin{array}{l}CH_3\\CH_3\end{array}\right\}O$	$-21°$
Methyl-ethyl ether	C_3H_8O	$\left.\begin{array}{l}CH_3\\C_2H_5\end{array}\right\}O$	$+12°$
Diethyl ether	$C_4H_{10}O$	$\left.\begin{array}{l}C_2H_5\\C_2H_5\end{array}\right\}O$	34°
Methyl-amyl ether	$C_6H_{14}O$	$\left.\begin{array}{l}CH_3\\C_5H_{11}\end{array}\right\}O$	92°
Ethyl-butyl ether	$C_6H_{14}O$	$\left.\begin{array}{l}C_2H_5\\C_4H_9\end{array}\right\}O$	80°
Ethyl-amyl ether	$C_7H_{16}O$	$\left.\begin{array}{l}C_2H_5\\C_5H_{11}\end{array}\right\}O$	112°
Dibutyl ether	$C_8H_{18}O$	$\left.\begin{array}{l}C_4H_9\\C_4H_9\end{array}\right\}O$	104°
Ethyl-hexyl ether	$C_8H_{18}O$	$\left.\begin{array}{l}C_2H_5\\C_6H_{13}\end{array}\right\}O$	132°
Diamyl ether	$C_{10}H_{22}O$	$\left.\begin{array}{l}C_5H_{11}\\C_5H_{11}\end{array}\right\}O$	176°

Ethane, or *Ethyl Hydride*, C_2H_6.—This hydrocarbon is obtained by heating zinc and methyl iodide in a closed tube to 150°:

$$2CH_3I + Zn = C_2H_6 = ZnI_2.$$

It may be obtained from ethyl iodide by heating it with zinc and water in sealed tubes to 150°:

$$2C_2H_5I + 2Zn + H_2O = 2C_2H_6 = ZnI_2 + ZnO.$$

The glass tubes containing these materials are heated in strong iron tubes placed in an air-bath (Fig. 77), provided with a thermometer.

Ethane is a colourless, tasteless gas, condensing to a liquid under a pressure of 46 atmospheres. It is rapidly acted on by chlorine in diffused daylight, yielding ethyl chloride, C_2H_5Cl. If excess of chlorine has been employed, a series of further chlorine substitution-products is obtained, the last of which is hexachlorethane, C_2Cl_6.

Ethyl Chloride, C_2H_5Cl, is obtained as a mobile liquid, having an ethereal, penetrating smell, by saturating alcohol with hydrochloric acid gas in presence of zinc chloride or by acting with the phosphorus chlorides upon alcohol :

$$5C_2H_5.OH + PCl_5 = 5C_2H_5Cl + H_3PO_4 + H_2O.$$

On heating the mixture, volatile ethyl chloride is given off, which must be condensed in a freezing mixture. Ethyl chloride boils at 12·5.

Phosphorus pentachloride acts in a similar manner on all alcohols, and indeed on all compounds containing the hydroxyl group. This reaction is therefore largely employed for ascertaining the presence or absence of this group in a compound, and also for determining how many such groups are present.

Ethyl Iodide, C_2H_5I, and *Ethyl Bromide*, C_2H_5Br, are obtained by acting upon alcohol with iodine and bromine in presence of phosphorus. The *iodide* is much used for the preparation of other ethyl compounds, owing to the facility with which the iodine can be exchanged in double decompositions. It is a heavy colourless liquid, boiling at 72°, and having a specific gravity of 1·946 at 16°.

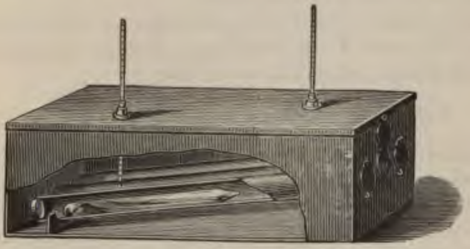


FIG. 77.

Ethyl Isocyanide, or *Ethyl Carbamine*, C_2H_5NC.—This substance is formed, together with its isomeride *propionitrile*, by acting on ethyl iodide with silver cyanide. It may also be prepared by heating a solution of ethylamine in alcohol with chloroform and caustic potash :

Ethylamine and	Chloroform yield	Ethyl Isocyanide and	Hydrochloric Acid.
$C_2H_5.NH_2$ +	$CHCl_3$ =	$C_2H_5.NC$ +	$3HCl$.

The boiling point of isocyanide of ethyl is 77°, and it possesses a very unpleasant, penetrating smell. It is decomposed by acids into ethylamine and formic acid.

Propionitrile.—The isomeric propionitrile, boiling at 97°, is prepared by distilling potassium ethyl-sulphate with potassium cyanide. It may be considered as a nitrogen compound (nitrile) of the next higher carbon series (propyl), for on heating with potash it yields propionic acid:

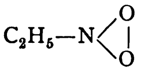
Propionitrile and Water yield Propionic Acid and Ammonia

$$C_2H_5.CN + 2H_2O = C_2H_5.COOH + NH_3.$$

Propionitrile, when acted upon by hydrogen, yields propylamine: $C_2H_5CN + 2H_2 = C_2H_5.CH_2NH_2$. These reactions are as already mentioned very important, for they are common to all the series of alcoholic nitriles, and enable us to pass from a lower to a higher carbon series—in this case from the 2- to the 3-carbon series.

Ethyl Nitrite, $C_2H_5NO_2$, is obtained as a sweet-smelling liquid, boiling at 18°, by distilling a mixture of alcohol, sulphuric acid and potassium nitrite thus:

$$C_2H_5HSO_4 + KNO_2 = C_2H_5NO_2 + KHSO_4.$$

When silver nitrite acts upon ethyl iodide, an isomeride termed *nitro-ethane* is formed, boiling at 113° and possessing a smell altogether different from ethyl nitrite. This substance has an acid reaction, and on treatment with an alcoholic solution of soda yields a compound $C_2H_4NaNO_2$. Nitro-ethane yields ethylamine when exposed to the action of nascent hydrogen. This reaction shows that the constitution of nitro-ethane is represented by  $C_2H_5{-}N\!<\!\begin{array}{c}O\\|\\O\end{array}$; while that of ethyl nitrite is $C_2H_5{-}O{-}N{=}O$, judging by its formation from an oxygen compound, *i.e.* alcohol.

If nitroethane be mixed with a solution of potassium nitrite (KNO_2) in caustic potash, and dilute sulphuric acid added, a deep red-coloured liquid is obtained. This reaction serves to distinguish the derivatives of a primary alcohol from those of a secondary or tertiary. For if the nitro-compound of a secondary alcohol be thus treated, a deep blue solution is obtained. The nitro-compounds derived from tertiary alcohols, on the other hand, yield colourless solutions when treated in a like manner, since they are quite unacted upon.

Ethyl Nitrate, $C_2H_5NO_3$, is formed by the action of nitric acid on alcohol when urea is present, as this body immediately destroys any nitrous acid which may be formed, and which otherwise causes the formation of ethyl nitrite and simultaneously oxidizes the alcohol present to aldehyde, &c., the reaction becoming extremely violent. It yields a vapour which is very explosive.

Ethyl Hydrosulphide, C_2H_5SH.—This compound, known as *Mercaptan*, is thio-alcohol, *i.e.* alcohol in which the oxygen is replaced by sulphur. It is obtained by acting on potassium hydrosulphide, HKS, with ethyl chloride, ethyl and potassium changing places. Mercaptan, like alcohol, can exchange its typical atom of hydrogen for metals : it forms with mercury an insoluble compound. Mercaptan boils at 36°, and possesses the nauseous, garlic-like smell characteristic of all the organic sulphur compounds.

Ethyl Sulphide $(C_2H_5)_2S$.—This compound in the sulphur series is analogous to ether in the oxygen series: it is obtained by acting on potassium sulphide, K_2S, with ethyl chloride. It is a colourless liquid, boiling at 91°, and possessing a strong disagreeable odour.

Hydrogen Ethyl-Sulphate, or *Ethylsulphuric Acid*, $C_2H_5O.SO_2.OH$, is formed when alcohol and strong sulphuric acid are mixed. It acts as an acid, and forms salts in which the typical hydrogen is replaced by a metal. The ethyl-sulphates of the alkalis and alkaline earths are soluble salts, and crystallize well.

Diethyl Sulphate, $(C_2H_5)_2SO_4$, is obtained by acting upon alcohol with ethyl chlorosulphonate; it is a body which decomposes on distillation and on addition of water.

Ethyl Phosphates are known: they correspond to the phosphates of the alkali-metals in containing either 1, 2, or 3 molecules of ethyl, replacing hydrogen in tribasic phosphoric acid. Thus we have:

Dihydrogen Ethyl-Phosphate.	Hydrogen Diethyl-Phosphate.	Triethyl Phosphate.
$\left.\begin{matrix}C_2H_5\\H_2\end{matrix}\right\}PO_4$;	$\left.\begin{matrix}C_2H_5\\C_2H_5\\H\end{matrix}\right\}PO_4$;	$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}PO_4$.

Ethyl Carbonate, $(C_2H_5)_2CO_3$, corresponding to sodium carbonate, Na_2CO_3, is prepared by acting upon silver carbonate with ethyl iodide. It is an aromatic liquid boiling at 126°.

Ethyl Cyanates.—Two ethyl cyanates are known. The true cyanate, $\left.\begin{matrix}C_2H_5\\CN\end{matrix}\right\}O$, is a thick, non-volatile liquid, formed by the action of cyanogen chloride on sodium ethylate. The isomeric compound, *ethyl isocyanate* or *ethyl carbimide*, $\left.\begin{matrix}C_2H_5\\CO\end{matrix}\right\}N$, is a colourless liquid, boiling at 60°, and possessing a powerful and irritating smell. It is formed by distilling potassium ethyl-sulphate with potassium cyanate. In contact with caustic potash it forms ethylamine:

$$\left.\begin{matrix}C_2H_5\\CO\end{matrix}\right\}N + 2\left.\begin{matrix}K\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_5\\H_2\end{matrix}\right\}N + \left.\begin{matrix}K\\K\end{matrix}\right\}CO_3.$$

Ethyl Borate, $\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}BO_3$, is a colourless liquid which burns with a bright green flame, and is obtained by acting on anhydrous alcohol with boron trichloride.

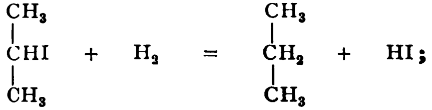
Ethyl Silicates.—Several ethyl compounds of silicic acid are obtained by the action of silicon tetrachloride upon alcohol. The compound $(C_2H_5)_4SiO_4$, corresponding to normal silicic acid, H_4SiO_4, is a volatile, colourless liquid, which burns, evolving a thick white smoke of silicon dioxide.

TRICARBON, OR PROPYL SERIES.

Primary Propyl Alcohol, $C_3H_7.OH$, has been found in the last products of distillation of French brandies; it boils at 97°, and is miscible in all proportions with water, but separates on addition of calcium chloride or other easily soluble salt. Propyl alcohol is acted upon by sulphuric acid with formation of hydrogen propyl-sulphate, $C_3H_7.HSO_4$. The propyl compounds closely resemble the foregoing ethyl series of bodies. Primary propyl alcohol, when oxidized, yields propionic acid, $C_2H_5CO.OH$, which is likewise formed from propionitrile (see p. 328).

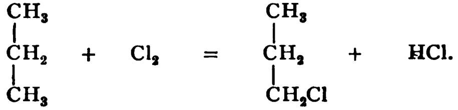
Secondary Propyl Alcohol, Isopropyl Alcohol, or *Dimethyl Carbinol,* $(CH_3)_2CH.OH$, boils at 84°, and is best prepared from isopropyl iodide, which is obtained by the action of hydriodic acid upon glycerol. From this isopropyl iodide we can prepare propane or propyl hydride by acting on it with zinc and dilute hydrochloric acid (1); this again on treatment with chlorine yields the primary propyl chloride (2); and this last, heated with acetate of sodium, gives propyl acetate, from which *primary* propyl alcohol can be obtained by the action of caustic potash. It is thus possible to obtain a primary from a secondary alcohol:

Isopropyl Iodide and Hydrogen yield Propane and Hydriodic Acid.

(1) 

$$\begin{array}{c} CH_3 \\ | \\ CHI \\ | \\ CH_3 \end{array} + H_2 = \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + HI;$$

Propane and Chlorine yield Normal Propyl Chloride. and Hydrochloric Acid.

(2) 

$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array} + Cl_2 = \begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2Cl \end{array} + HCl.$$

TETRACARBON, OR BUTYL SERIES.

By acting on ethyl iodide with zinc in a sealed tube at 150°, zinc iodide and a hydrocarbon, C_4H_{10}, called normal butane or butyl hydride, are formed.

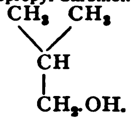
Normal Butane is a colourless liquid, boiling at + 1°, and is the lightest of all known liquids, having a specific gravity of only 0·600. This volatile hydrocarbon also exists in the light oils from American petroleum, as well as in coal oils. By the action of chlorine upon butane, butyl chloride can be obtained, and from this the alcohol itself has been prepared. This is the primary alcohol, as it yields on oxidation normal butyric aldehyde and butyric acid.

We have seen (p. 285) that two isomeric paraffins, C_4H_{10}, exist. Derived from these, four isomeric alcohols are known, 2 primary, 1 secondary, and 1 tertiary alcohol, viz.

(1)
Normal Butyl Alcohol, or Propyl Carbinol.

$CH_3.CH_2.CH_2.CH_2.OH.$

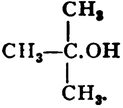
(2)
Isobutyl Alcohol, or Isopropyl Carbinol.



(3)
Methyl Ethyl Carbinol.

$CH_3.CH_2.CH(OH).CH_3.$

(4)
Tertiary Butyl Alcohol, or Trimethyl Carbinol.



$$\begin{array}{c} CH_3 \\ | \\ CH_3—C.OH \\ | \\ CH_3. \end{array}$$

(1) *Normal Butyl Alcohol* is also obtained by reduction of butyric acid. It possesses an alcoholic smell and boils at 116°·8.

(2) *Isobutyl Alcohol* is found in the fusel-oil from beet-root, potatoes, and grain. It boils at 109°.

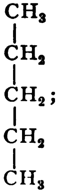
(3) *Methyl Ethyl Carbinol* is obtained from the corresponding iodide derived from erythrol (*v. infra*). It boils at 99°.

(4) *Trimethyl Carbinol* is contained in small quantities in fusel-oil, and is also formed by the action of acetyl chloride on zinc methyl. It is a white crystalline solid melting at 28° and boiling at 83°.

PENTACARBON SERIES.

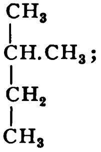
Three isomeric hydrocarbons containing five atoms of carbon exist:

(1)



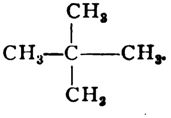
$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_2; \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

(2)



$$\begin{array}{l} CH_3 \\ | \\ CH.CH_3; \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

(3)



$$\begin{array}{c} CH_3 \\ | \\ CH_3—C——CH_3. \\ | \\ CH_3 \end{array}$$

Derived from these 3 hydrocarbons, 8 isomeric alcohols having the empirical formula $C_5H_{12}O$ can be obtained. Four of these are primary, 3 secondary, and 1 a tertiary alcohol.

Normal Pentane, C_5H_{12}, is found in petroleum and boils at 38°. When chlorine acts on the vapour of this hydrocarbon a mixture of primary and secondary pentyl chlorides is formed. This mixture when heated to 200° with potassium acetate gives two pentyl acetates, and these when boiled with potash yield the two alcohols.

Primary normal Pentyl Alcohol, or *Normal Amyl Alcohol*, $C_5H_{12}O$, B.P. 137°, is also obtained from pentylic acid by converting it first into the aldehyde and then into the alcohol.

Amyl Alcohol (*Isobutyl carbinol*) occurs commonly as the chief constituent of the fusel-oil obtained in the manufacture of potato brandy, from which it is obtained by washing with water and subsequent rectification. It is a colourless liquid, possessing a disagreeable, penetrating smell; it mixes in all proportions with alcohol and ether, but requires 50 parts of water at 13° for complete solution. Amyl alcohol boils at 131°·4, and solidifies at – 20°. It does not itself rotate the plane of polarized light but is always accompanied in the fusel-oil by another amyl alcohol (secondary butyl carbinol), which turns the plane to the left and boils at about 128°.

HIGHER ALCOHOLS AND THEIR COMPOUNDS.

Normal Hexyl Alcohol, $C_6H_{14}O$, is contained as a butyrate in the essential oil of *heracleum giganteum*; it boils at 157°. Theory points out the possible existence of seventeen isomerides, eight of which are now known. The corresponding hydrocarbon hexane is contained in large quantities, together with heptane, octane, &c., in American petroleum.

Heptyl Alcohol, $C_7H_{16}O$.—We know of five isomeric heptanes, C_7H_{16}; from these, thirty-eight possible isomerides of heptyl alcohol are derivable, and of these no less than thirteen are now known.

Octyl Alcohol, $C_8H_{18}O$, is contained as an acetate in the essential oil of the seeds of *heracleum sphondylium*. Secondary octyl alcohol, or methyl-hexyl-carbinol, is obtained by heating castor-oil with caustic potash.

The higher alcohols may be prepared from their hydrides or paraffins by acting upon the latter with chlorine, giving rise to the chlorides of the radicals; from the chlorides the acetates are prepared, and from the acetates the alcohols themselves.

Cetyl Alcohol, $C_{16}H_{34}O$, is found combined with palmitic acid in spermaceti. It forms a white solid crystalline mass, but behaves in all respects as an alcohol; thus it forms a chloride, $C_{16}H_{33}Cl$; also a bromide and iodide: it likewise yields an ether, $(C_{16}H_{33})_2O$, obtained by the action of cetyl iodide upon potassium cetylate; and a compound with sulphuric acid, $C_{16}H_{33}.HSO_4$. Cetyl alcohol undergoes oxidation when heated with caustic potash, yielding the corresponding acid in which one of oxygen replaces two of hydrogen of the alcohol:

$$\overset{\text{Cetyl Alcohol}}{C_{16}H_{33}OH} \overset{\text{and}}{+} \overset{\text{Potash}}{KOH} \overset{\text{yield}}{=} \overset{\text{Potassium Palmitate.}}{C_{16}H_{31}O_2K} \overset{\text{and}}{+} \overset{\text{Hydrogen.}}{2H_2}$$

This palmitic acid bears the same relation to cetyl alcohol as acetic acid does to common or ethyl alcohol.

Cerotyl Alcohol, $C_{27}H_{56}O$, is contained in Chinese wax: it is a white, solid, crystalline substance. When heated with potash it undergoes oxidation, and furnishes an acid called cerotic acid, $C_{27}H_{54}O_2$.

Melissyl Alcohol, $C_{30}H_{62}O$, is a solid white substance contained in beeswax: when fused with potash it forms an acid termed melissic acid, $C_{30}H_{60}O_2$.

LESSON XXXIII

COMPOUNDS DERIVED BY OXIDATION FROM THE ALCOHOLS

The general reactions which take place when the alcohols are oxidized have already been discussed in the introduction (p. 312). The following are the most important reactions, by means of which the monobasic acids can be obtained:

1. From the primary alcohol having the same number of carbon atoms, by direct oxidation.

2. From the primary alcohol containing one atom less carbon as follows:

(*a*) By decomposition of the alcoholic nitrile by potash; thus, propionitrile yields propionic acid.

(*b*) By acting with the sodium compound on carbon dioxide; thus, sodium-ethyl and carbon dioxide yield sodium propionate.

3. From ethyl acetoacetate $CH_3.CO.CH_2.CO_2C_2H_5$, and ethyl malonate $CH_2(CO_2C_2H_5)_2$ by a method which will be described in the chapter on organic synthesis.

MONOCARBON, OR FORMYL SERIES.

Formic Aldehyde, or *Formaldehyde*, CH_2O, is a colourless gas possessing a powerfully irritating smell. It is formed when the vapour of methyl alcohol together with air is led over a red-hot spiral of platinum wire. The aldehyde rapidly absorbs oxygen, and passes into formic acid.

Formic Acid, CH_2O_2.—This acid occurs ready formed in the bodies of red ants, whence its name; it is likewise found in stinging-nettles. Formic acid is obtained by the oxidation of methyl alcohol, as well as of sugar, starch, and other organic bodies. It is formed synthetically by acting upon potash with carbonic oxide gas at 100°:

$$\underset{\text{Carbon Monoxide}}{CO} \underset{\text{and}}{+} \underset{\text{Potash}}{HOK} \underset{\text{yield}}{=} \underset{\text{Potassium Formate.}}{CHO.OK.}$$

Also when carbon dioxide and aqueous vapour are acted on by potassium:

$$2CO_2 + K_2 + H_2O = CHO.OK + KHCO_3.$$

Formic acid, diluted with water, can be best prepared by heating crystallized oxalic acid with glycerol; monoformin, $CH_2(OCHO).CH(OH).CH_2.OH$, is first formed, and by the action of water this is converted into glycerol and formic acid:

$$\begin{aligned} &CH_2(OCHO).CH(OH).CH_2OH + H_2O \\ &\quad = CH_2(OH).CH(OH).CH_2.OH + H.COOH \end{aligned}$$

In order to obtain formic acid in the pure glacial state, free from water, dry crystallized lead formate is decomposed by a current of sulphuretted hydrogen gas, lead sulphide and formic acid being produced. Formic acid is a colourless liquid, possessing a peculiarly sharp smell and strong acid taste. It boils at 100°, and solidifies at a low temperature to a white crystalline mass melting at 8·6°: its specific gravity at 0° is 1·235, and it is miscible in all proportions with water. Heated with sulphuric acid, it forms water and pure carbonic monoxide, and oxidizing agents convert it easily into carbon dioxide and water. A formate, heated with excess of baryta, yields an oxalate:

Formic Acid yields Oxalic Acid and Hydrogen.

$$2\,CH_2O_2 = C_2H_2O_4 + H_2.$$

Formic acid is monobasic, and forms well-crystallized salts called *Formates*: all the formates are soluble in water. When ammonium formate is quickly heated it decomposes into hydrocyanic acid and water:

$$CHO.ONH_4 = CNH + 2H_2O;$$

whilst on the other hand hydrocyanic acid takes up water on continued standing, producing ammonium formate, so that hydrocyanic acid is the nitrile of formic acid. Formic acid may be distinguished from acetic acid by its power of reducing metallic mercury and silver as grey powders from their nitrates on boiling.

Formamide, $CHO.NH_2$.—Obtained by acting on ethyl formate with ammonia. It is a colourless liquid, boiling at 194° with partial decomposition.

DICARBON, OR ACETYL SERIES.

Acetic Aldehyde, or *Acetaldehyde*, C_2H_4O.—Acetaldehyde is obtained by oxidizing dilute alcohol with a mixture of potassium bichromate and sulphuric acid. It may also be prepared by distilling a dry mixture of acetate and formate of calcium:

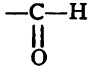
Acetic Acid and Formic Acid yield Aldehyde, Water, and Carbon Dioxide.

$$\left\{\begin{matrix} CH_3 \\ CO_2H \end{matrix}\right. + \left\{\begin{matrix} H \\ CO_2H \end{matrix}\right. = \left\{\begin{matrix} CH_3 \\ CHO \end{matrix}\right. + \left.\begin{matrix} H \\ H \end{matrix}\right\}O + CO_2.$$

Aldehyde is obtained as a by-product in the manufacture of spirit, where it comes over in the first runnings, and can be obtained perfectly pure by means of a rectifying column.

It is a colourless suffocating-smelling liquid, boiling at 21°; it has a specific gravity of 0·801 at 0°, and mixes in all proportions with water, alcohol, and ether. Aldehyde reduces metallic silver, in the form of a bright mirror, from solutions of the nitrate; and this reaction may be used to detect the presence of the substance, $C_2H_4O + Ag_2O = 2\ Ag + C_2H_4O_2$. It unites directly with nascent hydrogen to form alcohol, $C_2H_4O + H_2 = C_2H_6O$: it forms acetyl chloride when treated with chlorine, and acetic acid when acted upon by oxidizing agents. As its formula is C_2H_4O, it can no longer contain the ethyl group C_2H_5, nor does it contain the hydroxyl group, for when treated with phosphorus pentachloride we do not find that we get an OH group replaced by an atom of chlorine (p. 327), but instead the oxygen atom is replaced by two atoms of chlorine, forming the compound ethidene chloride $C_2H_4Cl_2$, which is also obtained by the action of chlorine or ethane. Now ethidene chloride has both chlorine atoms attached to the same carbon atom, and it would therefore appear that the oxygen atom they have replaced must be combined with one atom only. This leads us to the constitutional formula $CH_3.CO.H$, which also agrees very well with the other properties. Thus its reduction to alcohol and its oxidation to acetic acid are represented as follows

$$CH_3.CO.H + H_2 = CH_3.CH_2.OH$$
$$CH_3.CO.H + O = CH_3.CO.OH.$$



The group $-\underset{\underset{\textstyle O}{\|}}{C}-H$ or $-CH{=}O$ is characteristic of all aldehydes; it is however a group which readily undergoes change, and has an especial tendency to take up an atom of oxygen and pass into the carboxyl group, to which it owes the power of separating silver and mercury from solutions of their salts. It will be seen that this group also occurs in the formyl compounds just described, which accounts for the reducing action of these compounds.

Aldehyde is capable of existing in other forms, or of undergoing *polymeric* modifications. If it is preserved in contact with excess of acid, it remains unchanged; but if it be pure, it soon deposits a solid substance having the same composition as aldehyde, and termed *Metaldehyde*. This substance sublimes unchanged at 120°, but when heated to 200° in a closed tube it again forms aldehyde. *Paraldehyde* is another modification, and is a liquid boiling at 124°, having a vapour density of 4·58 corresponding to the molecular formula $C_6H_{12}O_3$, or $3(C_2H_4O)$. Aldehyde is also isomeric with ethylene oxide (p. 357). It forms a crystalline compound with ammonia, termed *aldehyde-ammonia*, $C_2H_4O.NH_3$, or $C_2H_4(OH).NH_2$, and, like other aldehydes, it also forms a crystalline compound, $C_2H_4O,NaHSO_3$, with acid sodium sulphite, which may be used for its separation from other bodies.

Chloral, $CCl_3.CHO$.—This substance may be considered as aldehyde, in which 3 of chlorine take the place of 3 of hydrogen, as trichloracetic acid is formed on its oxidation. It resembles aldehyde in many properties, such as forming a crystalline compound with ammonia, and reducing an ammonical silver solution. Chloral is obtained by the continued action of chlorine upon alcohol; it is a colourless, powerfully smelling liquid, boiling at 99°. With water, chloral forms *chloral hydrate*, $CCl_3.CH(OH)_2$, a solid crystalline substance now largely used in medicine for procuring quiet sleep. Its action possibly depends upon the fact that in presence of the alkalis contained in the blood chloral hydrate gradually changes to chloroform:

$$CCl_3.CHO + KOH = CHCl_3 + CHO.OK.$$

Chloral and potash give chloroform and potassium formate.

Acetic Acid, $C_2H_4O_2$.

Dilute acetic acid has been known as vinegar from very early times; it occurs in the juices of certain plants and vegetables, but only in small quantities. The most important modes of preparing acetic acid are: (1) the method generally practically employed, by the oxidation of alcohol; (2) the theoretically interesting processes—1st, by the direct combination of carbon dioxide and sodium methyl:

$$CH_3Na + CO_2 = CH_3.CO_2Na.$$

and 2nd, by the action of potash on acetonitrile:

$$CH_3.CN + 2H_2O = CH_3.CO.OH + NH_3.$$

(3) Acetic acid is also prepared on a large scale by the dry distillation of wood; the crude acid thus obtained is commonly called *Pyroligneous acid.*

The process by which alcoholic liquids (beer or wine) yield acetic acid on oxidation is termed the *Acetous Fermentation* (see later, under Fermentation) : the liquids are exposed to the air at a temperature of about 25° for a fortnight, when the alcohol is changed to vinegar. This change is brought about by the presence of a peculiar vegetable growth (*mycoderma aceti*), which floats on the surface of the liquid, first absorbing the oxygen, and then giving it up to the alcohol.

Acetic acid in the pure state is obtained by heating sodium acetate with strong sulphuric acid; it is a colourless liquid, boiling at 118° and solidifying to an icelike mass at 17°; hence the name of *glacial acetic acid* has been given to it. It possesses a peculiar sharp smell, and has a strong acid taste; it mixes in all proportions with water, but when distilled the mixture has no definite boiling point; the residue becomes stronger until glacial acid remains. Acetic acid may be recognized by its smell, and by the formation of ethyl acetate; also by the production of cacodyl (p. 348) when an acetate is heated with arsenic trioxide. Acetic acid is mono-basic, and forms a series of well-defined salts termed *Acetates.* The acetates of the alkalis are soluble crystallizable salts. Aluminium and ferric acetates are soluble compounds used in large quantities as mordants by dyers and calico-printers under the commercial names of *Red Liquor* and *Iron Liquor. Lead acetate*, or sugar of lead, and *copper acetate*, or verdigris, are the most important compounds of acetic acid with the heavy metals. The radicals methyl and ethyl, &c., can be substituted for the atom of typical hydrogen in acetic acid, forming the ethereal salts.

Ethyl Acetate, $C_2H_5O.C_2H_3O$, is prepared by distilling an acetate with a mixture of sulphuric acid and alcohol. It is a colourless pleasant-smelling liquid, boiling at 77°.

Amyl Acetate, $C_5H_{11}O.C_2H_3O$, is prepared by distilling common amyl alcohol with sodium acetate and sulphuric acid. It boils at 137°, and has a smell resembling that of Jarganelle pears, and is therefore used as a flavouring for cheap confectionery.

Acetyl Chloride, C_2H_3OCl, is obtained by the action of phosphorus trichloride upon acetic acid:

$$2PCl_3 + 3C_2H_3O.OH = P_2O_3 + 3C_2H_3O.Cl + 3HCl.$$

It is a colourless liquid, fuming strongly in the air, and boiling at 50·9°. Like other acid chlorides it is quickly decomposed by water, yielding acetic and hydrochloric acids; treated with alcohols, it yields the acetates, for the preparation of which it is frequently used. The corresponding bromide and iodide are known.

Acetyl Oxide, $(C_2H_3O)_2O$, or *Acetic Anhydride*, is a colourless liquid, boiling at 138°, formed by the action of phosphorus oxychloride, or acetyl chloride, upon sodium acetate;

$$4C_2H_3O_2Na + POCl_3 = 2(C_2H_3O)_2O + 3NaCl + NaPO_3$$

It forms with water two molecules of acetic acid.

Chloracetic Acids.—Chlorine acts upon acetic acid, replacing one, two, or three atoms of the hydrogen of the radical acetyl by chlorine; we thus obtain *monochloracetic acid*, $CH_2Cl.COOH$; *dichloracetic acid*, $CHCl_2.COOH$; and *trichloracetic acid*, $CCl_3.COOH$. These three bodies are crystalline solids: the first fuses at 62°, and boils at 186°; the second boils at 191°, whilst the third melts at 52·3° and boils at 195°. They form salts analogous to the acetates, and yield acetic acid by the action of nascent hydrogen.

Thiacetic Acid, $C_2H_3O.SH$.—This substance stands to acetic acid in the same relation as mercaptan to alcohol (p. 329); it is prepared by the action of pentasulphide of phosphorus on acetic acid.

$$P_2S_5 + 5C_2H_4O_2 = P_2O_5 + 5C_2H_3O.SH.$$

It is a colourless liquid, possessing a peculiarly nauseous smell, and boiling at 93°. The anhydride, $(C_2H_3O)_2S$, is also known.

Acetyl Peroxide, $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O_2$, is a remarkable compound obtained by the action of barium dioxide upon acetyl oxide. It is a thick liquid, possessing energetic oxidizing properties, and on heating decomposes with explosive violence.

Acetamide, $C_2H_3O.NH_2$, is obtained by the action of ammonia upon ethyl acetate by an exchange of acetyl for hydrogen:

$$\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}O + \left.\begin{matrix}H\\H\\H\end{matrix}\right\}N = \left.\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right\}N + \left.\begin{matrix}H\\C_2H_5\end{matrix}\right\}O.$$

It is also formed by the action of ammonia on acetyl chloride, and by the dry distillation of ammonium acetate. Acetamide is a colourless solid, melting at 78° and boiling at 222°.

Diacetamide, $NH(C_2H_3O)_2$, and *Triacetamide*, $N(C_2H_3O)_3$, are also known. Corresponding compounds are likewise formed from the chloracetic acids.

The Fulminates

are compounds of fulminic acid, a body which has not yet been isolated, whose constitution is as yet uncertain. Silver fulminate, $Ag_2C_2N_2O_2$, is formed by the action of alcohol on a solution of silver in nitric acid:

$$C_2H_6O + 2AgNO_3 + N_2O_3 = Ag_2C_2N_2O_2 + 2HNO_3 + 2H_2O.$$

It crystallizes in small white needles which explode most violently on heating or on percussion. *Mercury fulminate*, $HgC_2N_2O_2$, is prepared on the large scale by dissolving mercury in nitric acid and adding alcohol. It is a very dangerous substance, and is used for filling percussion caps.

Acetone, or Dimethyl Ketone,

$CO\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$.—This compound is formed by the oxidation of secondary propyl alcohol, as well as by replacing the chlorine in acetyl chloride by methyl:

$$(CH_3)_2Zn + 2C_2H_3O.Cl = 2C_2H_3O.CH_3 + ZnCl_2.$$

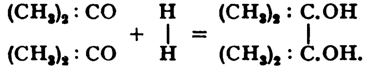
It is also obtained by the distillation of calcium acetate, or by passing the vapour of acetic acid through a red-hot tube.

$$2CH_3.CO.OH = CH_3.CO.CH_3 + H_2O + CO_2.$$

Acetone is a colourless liquid, boiling at 56°, and forming, like aldehyde, a crystallizable compound with hydrogen sodium sulphite. By the action of sodium amalgam on a mixture of water and acetone, two atoms of hydrogen are taken up, and secondary propyl alcohol is formed (p. 331):

$$CH_3.CO.CH_3 + H_2 = CH_3.CH(OH).CH_3.$$

Under certain conditions, however, the reaction takes place in a different manner, two molecules of acetone uniting in the following manner forming a substance termed *pinacone:*



$$\begin{array}{l} (CH_3)_2 : CO \\ (CH_3)_2 : CO \end{array} + \begin{array}{c} H \\ | \\ H \end{array} = \begin{array}{l} (CH_3)_2 : C.OH \\ \qquad\quad | \\ (CH_3)_2 : C.OH. \end{array}$$

Ketones may also be prepared synthetically from ethyl acetoacetate, in a manner which will be described in the chapter on organic synthesis.

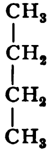
HIGHER FATTY ACIDS.

The names, composition, and boiling points of these acids have already been given (p. 315). In their general characteristics they closely resemble the first two of the series, formic acid and acetic acid. They occur in many natural fats, in combination with glycerol, from which they are separated by treatment with alkalis, whereby salts of the fatty acids (soaps) and glycerol are formed.

These acids may be prepared synthetically by the following important reactions: (1) by the direct combination of carbon dioxide with the sodium compound of the next lower alcohol radical (p. 338); (2) by the action of potash on the cyanide of the next lower alcohol radical (p. 338); and (3) from ethyl acetoacetate and ethyl malonate in the manner described in the chapter on organic synthesis. Those containing less than ten atoms of carbon are for the most part oily liquids slightly soluble in water, easily in alcohol, and each forms a well-defined series of salts. The higher members of the series, especially palmitic and stearic acids, occur in all fatty bodies; they are solid substances and are obtained by decomposing soaps made from palm-oil or beef-suet, which consist of sodium or potassium palmitate and stearate (see Fats). These acids form anhydrides, compound ethers, chlorides, aldehydes, amides, and ketones, corresponding in constitution and in general chemical character with the same compounds in the acetyl series. For the description of the properties of these compounds the third volume of the *Treatise on Chemistry*[1] must be consulted.

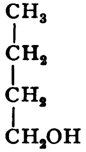
It is, however, necessary to remember that a large number of isomeric compounds exist in the acid as well as in the alcohol series. These iso-acids are derived from the corresponding primary iso-alcohols. The isomeric hydrocarbons, alcohols, and acids of the 4-carbon series, are as follows:

Normal Butane.



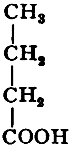
$CH_3-CH_2-CH_2-CH_3$

Normal Butyl Alcohol.



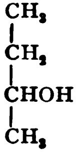
$CH_3-CH_2-CH_2-CH_2OH$

Normal Butyric Acid.



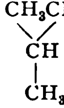
$CH_3-CH_2-CH_2-COOH$

Secondary Butyl Alcohol.



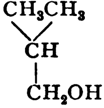
$CH_3-CH_2-CHOH-CH_3$

Isobutane. (Trimethyl methane).



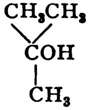
$(CH_3CH_3)CH-CH_3$

Fermentation Butyl Alcohol.



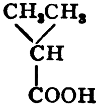
$(CH_3CH_3)CH-CH_2OH$

Tertiary Butyl Alcohol.



$(CH_3CH_3)COH-CH_3$

Isobutyric Acid.



$(CH_3CH_3)CH-COOH$

Butyric Acid, $C_4H_8O_2$, is found together with other fatty acids combined with glycerol in butter. It is best prepared by the fermentation of sugar mixed with putrid cheese and chalk. It boils at 163°.

Ethyl butyrate, $C_4H_7O_2.C_2H_5$ has a pleasant fruit-like odour, and is used as a flavouring for cheap confectionery and rum.

Isobutyric Acid, $(CH_3)_2CH.COOH$, boils at 155°. It occurs in the carob bean, and is prepared by the oxidation of isobutyl alcohol, or by acting on isopropyl iodide with potassium cyanide, and treating the nitrile thus obtained with caustic potash.

$(CH_3)_2CH.I$	$(CH_3)_2CH.CN$	$(CH_3)_2CH.COOH$
Isopropyl iodide.	Isobutyronitrile.	Isobutyric acid.

Valeric Acid, $C_5H_{10}O_2$, occurs in Valerian root. It can be prepared by oxidizing fermentation amyl alcohol with chromic acid, or by acting on potassium isobutylsulphate with potassium cyanide, and treating the valeronitrile thus obtained with caustic potash. Valeric acid is therefore isopentylic acid $(CH_3)_2CH.CH_2.COOH$.

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[1] *Treatise on Chemistry*, by Roscoe and Schorlemmer, vol. iii. part i. pp. 560-695 (Macmillan and Co.).

Palmitic Acid, $C_{16}H_{32}O_2$, and *Stearic Acid*, $C_{18}H_{36}O_2$, are the most important of the remaining members of this series; their compounds with glycerol form the chief constituent of solid fats. The ordinary stearin candles consist almost entirely of a mixture of these two acids.

LESSON XXXIV

COMPOUNDS OF THE ALCOHOL RADICALS WITH THE NITROGEN (TRIAD) GROUP OF ELEMENTS.—N. P. As. Sb. Bi.

Nitrogen Bases

Compound Alcoholic Ammonias.—The constitution of the primary monamines, as *Ethylamine*, $C_2H_5NH_2$; secondary monamines, as *Diethylamine*, $(C_2H_5)_2NH$, and tertiary monamines, as *Triethylamine*, $(C_2H_5)_3N$, have already been mentioned (p. 311). These bodies are volatile without decomposition; they all have a strong alkaline reaction and ammoniacal smell, and combine with HCl, &c., to form salts. These compound ammonias are formed in many ways, of which the most important are—

1. By the action of caustic alkalis on the iso-cyanates of the alcohol radicals (see p. 330).

2. By the direct combination of the nitriles with nascent hydrogen; thus acetonitrile yields propylamine:

$$C_2H_5.CN + 2H_2 = C_2H_5.CH_2.NH_2.$$

3. By the action of the iodides of the alcohol radicals on ammonia, we obtain the iodide of the compound-ammonium, which, when treated with potash, yields the compound ammonia:

$$\overset{\text{Ethyl iodide and Ammonia give}}{C_2H_5I + NH_3} = \overset{\text{Ethylammonium iodide.}}{C_2H_5.NH_2,HI.}$$

Ethyl iodide acts similarly on ethylamine, giving rise to diethylammonium iodide :

$$C_2H_5I + C_2H_5.NH_2 = (C_2H_5)_2NH,HI ;$$

and also acts upon diethylamine in the same way, giving rise to triethylammonium iodide :

$$C_2H_5I + (C_2H_5)_2HN = N(C_2H_5)_3HI.$$

Ethyl iodide also combines with triethylamine to form tetra-ethyl-ammonium iodide, $N(C_2H_5)_4I$. The above reactions do not, however, occur in the simple manner here described, for all these compounds are formed together when ethyl iodide acts on ammonia. The compounds of mono-, di-, and tri-ethylamine with hydriodic acid are decomposed by caustic potash, and the volatile compound ammonias liberated. The case of the tetra-ethyl-ammonium iodide is different, as it is not decomposed by potash, but yields, when treated with moist silver oxide, a hydrated oxide, which does not volatilize without decomposition, and is analogous in constitution and similar in properties to caustic potash :

Tetra-ethyl-ammonium Hydroxide.	Potassium Hydroxide.
$(C_2H_5)_4N(OH)$.	$K(OH)$.

By acting on ethylamine with other iodides, such as methyl iodide, mixed amines can be prepared. The hydrochlorides of compound ammonias form more or less insoluble double salts with platinic chloride ; the larger the number of organic radicals contained, the more soluble is the platinum salt. Their sulphates also form alums with aluminium sulphate, which are isomorphous with ordinary alum.

4. By acting on acid amides, such as acetamide, $CH_3.CO.NH_2$ with bromine, adding caustic potash and distilling, the amide is first converted into the bromamide $CH_3.CO.NHBr$, which loses hydrogen bromide forming the isocyanate :

$$CH_3.CO.NHBr - HBr = CO : N.CH_3.$$

the latter is then decomposed by caustic potash in the manner already described in (1).

$$CO : N.CH_3 + H_2O = CO_2 + CH_3.NH_2.$$

Methylamine, CH_3NH_2, occurs in herring brine, and may be obtained by the action of nascent hydrogen on prussic acid. It is a colourless, condensible gas, possessing a strong ammoniacal smell and powerful alkaline reaction. 1,000 volumes of this gas dissolve in one volume of water at 15°, so that it is even more soluble than ammonia. It closely resembles ammonia, but may be distinguished from it by being readily inflammable, burning with a yellow flame. Methylamine is now made on a large scale by distilling the *vinasse* or residue left in the manufacture of beet-root sugar. It is chiefly used for preparing methyl chloride, which is employed in the manufacture of coal tar colouring matters.

Dimethylamine, $(CH_3)_2NH$, is also a colourless gas, smelling like ammonia, and liquefying at +8°

Trimethylamine, $(CH_3)_3N$, boils at 9°·3, and has a strong ammoniacal and fish-like smell. It occurs in the flowers of certain plants, such as the hawthorn and pear, as well as in many animal fluids, particularly in herring-brine. It combines with methyl iodide to form *tetramethylammonium iodide*, $(CH_3)_4 NI$. If to this we add freshly precipitated silver oxide, a strongly caustic solution of *tetramethylammonium hydroxide*, $(CH_3)_4N.OH$, is obtained.

Trimethylamine is metameric with methylethylamine and propylamine. These metameric bodies can be distinguished by ascertaining how many atoms of the replaceable hydrogen of the original ammonia they contain.

The ethylamines closely resemble the foregoing compounds. Ethylamine, $(C_2H_5)NH_2$, boils at 18°·7; diethylamine, $(C_2H_5)_2NH$, at 57°; and triethylamine, $(C_2H_5)_3N$, at 91°.

Thiocarbimides.—When a primary amine is brought together with carbon disulphide a thiocarbimic acid is formed: the silver salt of this acid when heated with water yields a thiocarbimide:

$$2CS\left\{\begin{matrix}SAg\\NHCH_3\end{matrix}\right. = 2N\left\{\begin{matrix}CH_3\\CS\end{matrix}\right. + Ag_2S + H_2S.$$

Methyl thiocarbimide is a white crystalline mass melting at 34° and boiling at 119°. These compounds are also termed *mustard-oils*, because the similar compound of the radical *allyl* (*v. infra*) is the oil of mustard, and all these bodies have a sharp smell resembling mustard.

Phosphorus Bases.

Phosphine, PH_3, possesses only feeble basic powers, and the compound it forms with hydriodic acid, PH_4I, readily decomposes. But by replacing the hydrogen in phosphine by alcohol radicals, this body yields stable compounds corresponding to the amines. These are the phosphorus bases or phosphines. They are divided into primary, secondary, and tertiary compounds: thus *triethylphosphine*, $P(C_2H_5)_3$, is obtained by acting upon zinc ethyl with phosphorus trichloride, the chlorine changing places with ethyl.

Triethylphosphine is a colourless liquid, boiling at $127^{\circ}\cdot5$, and possessing a powerful and disagreeable smell. It combines directly with oxygen, sulphur, and chlorine, in this respect differing from the foregoing nitrogen bases. With ethyl iodide it combines and forms iodide of tetra-ethyl-phosphonium iodide, $P(C_2H_5)_4I$, from which a strongly caustic hydroxide, analogous to the corresponding nitrogen compound, can be obtained by the action of silver oxide.

The other compound phosphorus bases, viz: *Ethyl phosphine*, $C_2H_5.PH_2$, and *diethyl phssphine*, $(C_2H_5)_2PH$, have been obtained by a different reaction, viz., by acting upon phosphonium iodide, PH_4I, with ethyl iodide in presence of zinc oxide. Both the above compounds are formed simultaneously in combination with hydriodic acid:

$$(1)\ ZnO + 2C_2H_5I + 2PH_4I = 2(C_2H_5.PH_2.HI) + ZnI_2 + H_2O.$$
$$(2)\ ZnO + 2C_2H_5I + PH_4I = (C_2H_5)_2PH.HI + ZnI_2 + H_2O.$$

The mixture is sealed up in glass tubes and heated for several hours to 150°, when a crystalline mass is formed. By the action of water upon the crystalline mass the *ethyl phosphine* is liberated as a volatile colourless liquid boiling at 25° and possessing a most powerful and nauseous odour: the further action of alkalis liberates the *diethyl phosphine*. This is also a colourless liquid, boiling at 85°, and possessing a strong smell, different from that of the preceding compound. Both these phosphines combine with the greatest avidity with acids, and also with oxygen and sulphur, to form definite compounds.

Methyl phosphine, CH_3PH_2, has also been prepared; at the ordinary temperature it is a colourless gas, in this respect resembling phosphuretted hydrogen, PH_3.

The following table shows the similarity between amines and phosphines:

Amines.	Ammonium iodide	NH_4I.
	Monethylammonium iodide	$N(C_2H_5)H_3I$.
	Diethylammonium ,,	$N(C_2H_5)_2H_2I$.
	Triethylammonium ,,	$N(C_2H_5)_3HI$.
	Tetraethylammonium ,,	$N(C_2H_5)_4I$.
Phosphines.	Phosphonium iodide	PH_4I.
	Monethylphosphonium iodide	$P(C_2H_5)H_3I$.
	Diethylphosphonium ,,	$P(C_2H_5)_2H_2I$.
	Triethylphosphonium ,,	$P(C_2H_5)_3HI$.
	Tetraethylphosphonium ,,	$P(C_2H_5)_4I$.

Arsenic Bases.

The compounds of arsenic with the alcohol radicals differ somewhat in constitution from the foregoing, inasmuch as we are acquainted in the methyl series with compounds of the following; (1) *trimethylarsine*, $(CH_3)_3As$; (9) *arsendimethyl*, $(CH_3)_2As$; (3) *arsenmonomethyl*, CH_3As. The first of these is constructed on the type of ammonia, and the two latter combine directly with one and two atoms of chlorine respectively, and then form compounds belonging to the general type, NH_3. We thus have the following compounds known:

Arsenic trihydride	AsH_3.
Trimethylarsine	$As(CH_3)_3$.
Arsendimethyl chloride	$As(CH_3)_2.Cl$.
Arsenmonomethyl dichloride	$AsCH_3.Cl_2$.
Arsenic trichloride	$AsCl_3$.

Trimethylarsine is a colourless liquid, boiling at 120°, formed by the action of methyl iodide on an alloy of sodium and arsenic; it corresponds to trimethylamine and trimethyl phosphine.

Arsendimethyl or *Cacodyl*, $As_2(CH_3)_4$.—This substance, together with its oxide, $(CH_3)_2As.O.As(CH_3)_2$, is formed on heating arsenic trioxide with potassium acetate and an alkali. Cacodyl is a colourless liquid, boiling at 170°, which takes fire in contact with the air. It is extremely poisonous, and possesses a most disagreeable, garlic-like smell, and must be prepared with great care. It combines with chlorine, oxygen, &c., and plays the part of an organo-metallic radical. Free cacodyl is $As_2(CH_3)_4$, but the monad radical which enters into combination is only half this, viz., $(CH_3)_2As$. One of the most important compounds is cacodylic acid, $(CH_3)_2AsO(OH)$; it is soluble in water, and is not poisonous. The formation of cacodyl and its oxide, in the mode described, may be used as a delicate test for the presence of arsenic, from the strong and characteristic odour of this body.

Antimony-Bases.—By acting on ethyl iodide with an alloy of antimony and potassium, a compound called *triethylstibine*, $(C_2H_5)_3Sb$, has been prepared; it is a colourless liquid, boiling at 158°, which takes fire and burns in contact with the air. It forms compounds with oxygen, sulphur, and chlorine.

Bismuth forms an analogous compound, *triethylbismuthine*, $(C_2H_5)_3Bi$.

COMPOUNDS OF ALCOHOL RADICALS WITH OTHER ELEMENTS.

Sodium-ethyl, NaC_2H_5, has not isolated, but forms the double compound, $NaC_2H_5 + Zn(C_2H_5)_2$. As already mentioned it is converted by carbon dioxide on heating into sodium propionate.

$$C_2H_5Na + CO_2 = C_2H_5.CO_2Na.$$

Zinc-ethyl, $Zn(C_2H_5)_2$. This substance, which is the most important of the organo-metallic compounds, is obtained by the action of zinc on ethyl iodide; the first action is the formation of a non-volatile crystalline compound of the two substances, which when more strongly heated decomposes as follows:

$$2C_2H_5ZnI = ZnI_2 + Zn(C_2H_5)_2.$$

It is a colourless liquid, boiling at 118°, and takes fire spontaneously on exposure to air or oxygen, burning with a greenish flame; on slow oxidation it yields *zinc ethylate*, $Zn(OC_2H_5)_2$. Zinc ethyl is a most valuable reagent, and is used for the preparation of many other compounds of alcohol radicals with the elements. *Zinc-methyl* and *Zinc-amyl* are also known.

Mercuric-ethyl, $Hg(C_2H_5)_2$, is prepared by treating mercuric chloride with zinc ethyl, or by the action of sodium amalgam on ethyl iodide containing ethyl acetate.

$$Hg + Na_2 + 2C_2H_5I = Hg(C_2H_5)_2 + 2NaI.$$

The action of the ethyl acetate is at present unexplained; it may be recovered unaltered at the end of the operation. Mercuric-ethyl is a colourless liquid which boils at 159°, and a deadly poison.

Boron-triethyl, $B(C_2H_5)_3$, is obtained by acting on ethyl is borate with zinc-ethyl.

$$2(C_2H_5O)_3B + 3Zn(C_2H_5)_2 = 2(C_2H_5)_3B + 3Zn(OC_2H_5)_2.$$

It is a colourless liquid boiling at 95°, possesses a very powerful acrid smell, and takes fire on exposure to the air, burning with a green flame.

Silicon-ethyl, $(C_2H_5)_4Si$, is obtained by the action of zinc-ethyl on silicon tetrachloride: it is a colourless liquid which boils at 150°, and is not attacked by nitric acid. It is acted on by chlorine, a monochlorinated product, $SiC_8H_{19}Cl$, being first obtained. This substance acts as the chloride of a monad radical: thus when heated with acetate of potash it yields an acetate, and this on treatment with potash forms a colourless liquid smelling like camphor, and acting as an alcohol, having the formula $SiC_8H_{20}O$. Hence silicon-ethyl may be regarded as a nonyl hydride, C_9H_{20}, in which one atom of (tetrad) carbon has been replaced by one of (tetrad) silicon.

Nonyl hydride	$C(C_2H_5)_4$.
,, chloride	$C(C_2H_5)_3(C_2H_4Cl)$.
,, acetate	$C(C_2H_5)_3(C_2H_4O.C_2H_3O)$.
,, alcohol	$C(C_2H_5)_3(C_2H_4.OH)$.

		B.P.
Silico-nonyl hydride . . .	$Si(C_2H_5)_4$	150°
,, chloride . .	$Si(C_2H_5)_3(C_2H_4Cl)$	187°
,, acetate . . .	$Si(C_2H_5)_3C_2H_4O.C_2H_3O)$	211°
,, alcohol . . .	$Si(C_2H_5)_3(C_2H_4.OH)$.	

A substance having the composition $SiHCl_3$ has also been prepared. This body, it will be seen, is chloroform, $CHCl_3$, in which silicon replaces carbon, and is termed *silicochloroform.*

Tin tetra-ethyl, $Sn(C_2H_5)_4$, is a volatile liquid boiling at 181°, obtained by the action of tin tetrachloride upon zinc-ethyl.

Tin triethyl, $Sn_2(C_2H_5)_6$ is formed together with the following compound when ethyl iodide acts on an alloy of 20 parts of sodium, and 80 parts of tin. It boils at 175—180°.

Tin diethyl, $Sn_2(C_2H_5)_4$ is a yellow oily liquid, which decomposes on heating into tin, and tin tetra-ethyl.

Lead tetra-ethyl, $Pb(C_2H_5)_4$, is a heavy liquid, boiling at 200°.

Lead tri-ethyl, $Pb_2(C_2H_5)_6$, is obtained by heating ethyl iodide with an alloy of lead and sodium. The existence of these two compounds points out that lead acts as a tetrad towards positive radicals. In its compounds with negative elements, lead, however, acts as a dyad, as the vapour density of lead chloride shows that its molecular formula is $PbCl_2$. In lead tri-ethyl two atoms of metal are supposed to be connected by one combining unit.

GENERAL REACTIONS OF MONAD ALCOHOLS AND ACIDS.

The general reactions of these groups which offer the greatest theoretical interest, are certainly those by which it is possible, in the first place, to prepare the most simple terms of the series synthetically from their elements, and, secondly to pass directly by addition of carbon and hydrogen from these lower terms to the higher ones, and thus to mount up the series. Suppose that we begin with methyl alcohol obtained from inorganic sources ; viz.—

(1) Marsh gas prepared from sulphuretted hydrogen and carbon disulphide :

$$2SH_2 + CS_2 + 4Cu_2 = CH_4 + 4Cu_2S.$$

(2) Methyl chloride, from this by the action of chlorine :

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

(3) Methyl alcohol, from this by the action of potash :

$$CH_3Cl + KOH = CH_3OH + KCl.$$

There are now several methods by which we can pass to the dicarbon series :—

(1) From methyl alcohol we prepare acetonitrile. This, on decomposition with potash, yields potassium acetate (see p. 339) :

$$CH_3.CN + KOH + H_2O = CH_3COOK + NH_3.$$

We can also directly reduce the acids to aldehydes by heating them with a salt of formic acid ; and from aldehyde we can obtain ethyl alcohol directly by the action of hydrogen (p. 337) :

$$C_2H_4O + H_2 = C_2H_6O.$$

(2) From methyl alcohol we prepare methyl cyanide, and by acting upon this with hydrogen we get ethylamine (p. 346) :

$$CH_3.CN + 2H_2 = CH_3.CH_2.NH_2.$$

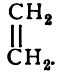
Ethylamine when acted on by nitrous acid is converted into ethyl alcohol :

$$C_2H_5.NH_2 + HNO_2 = C_2H_5.OH + H_2O + N_2.$$

(3) From methyl alcohol, by the action of zinc on methyl iodide, we prepare the ethyl hydride or ethane : this substance forms ethyl chloride when treated with chlorine : from this we can pass through ethyl acetate to ethyl alcohol. The repetition of any of these three processes would enable us to pass to the tricarbon group, and so on.

LESSON XXXV

DERIVATIVES OF DYAD ALCOHOL RADICALS

WE have already seen (p. 280) that a series of hydrocarbons runs parallel with the paraffins, containing two atoms less hydrogen, and having therefore the general formula C_nH_{2n} ; and further it has been stated that in these hydrocarbons it is usually supposed that two of the carbon atoms are connected together by two combining units, ethylene C_2H_4 being represented by the formula  $\begin{array}{l}CH_2\\ \|\\ CH_2.\end{array}$

These hydrocarbons are formed from the alcohols of the monovalent radicals, by removing the elements of water with sulphuric acid or zinc chloride :

$$C_2H_6O - H_2O = C_2H_4.$$

They may also be prepared from the compounds of the alcohol radicals with halogens by the action of alcoholic potash :

$$C_4H_9Cl + KOH = C_4H_8 + KCl + H_2O.$$

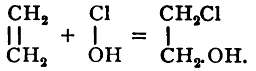
They occur further, together with paraffins, in the products of distillation of many organic substances, and are therefore contained in wood and coal-tar.

The names of the olefines are derived from those of the corresponding monovalent alcohol radicals by adding the syllable " ene " ; thus the hydrocarbon C_2H_4, obtained from ethyl alcohol or chloride receives the name " Ethylene."

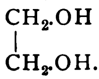
The olefines are distinguished from the paraffins inasmuch as they readily pass into saturated compounds by direct addition of other elements or radicals. Thus ethylene unites with hydriodic acid forming ethyl iodide :

$$C_2H_4 + HI = C_2H_5I.$$

This addition takes place especially easily with chlorine and bromine, which yield compounds of divalent radicals, such as ethylene bromide $C_2H_4Br_2$. The olefines may therefore be regarded as divalent radicals in the free state ; they combine also with hypochlorous acid, ClOH, forming compounds which are simultaneously chlorides and alcohols, and are termed therefore *chlorhydrins* :



$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + \begin{array}{l}Cl\\ |\\ OH\end{array} = \begin{array}{l}CH_2Cl\\ |\\ CH_2.OH.\end{array}$$

If in the haloid compounds we replace both halogen atoms by hydroxyl we get the alcohols of the divalent radicals, which are known as *glycols*, such as ethylene glycol,  $\begin{array}{l}CH_2.OH\\ |\\ CH_2.OH.\end{array}$ The hydroxyl groups in these compounds may be replaced singly by other radicals, giving rise to "mixed" derivatives, of which the above chlorhydrin may be taken as an example.

The following table contains a list of the best known olefines and glycols.

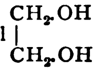
		B.P.			B.P.
Ethylene	C_2H_4	—	Ethylene glycol	$C_2H_4(OH)_2$	197°·5
Propylene	C_3H_6	—	Propylene glycol	$C_3H_6(OH)_2$	188°
Butylene	C_4H_8	−5°	Butylene glycol	$C_4H_8(OH)_2$	216°
Isobutylene		−6°	Isobutylene glycol		183°
Pentylene	C_5H_{10}	39°	—		—
Amylene		30°	Amylene glycol	$C_5H_{10}(OH)_2$	177°
Hexylene	C_6H_{12}	70°	Hexylene glycol	$C_6H_{12}(OH)_2$	207°
Heptylene	C_7H_{14}	100°	—		—
Isoheptylene		91°	—		—
Octylene	C_8H_{16}	125°	Octylene glycol	$C_8H_{16}(OH)_2$	237°
Diamylene	$C_{10}H_{20}$	160°	—		—
Cetylene	$C_{16}H_{32}$	275°	—		—

The initial member of the series of hydrocarbons, methylene CH_2, does not exist in the free state, but derivatives such as CH_2Cl_2 and $CH_2(OC_2H_3O)_2$ are known.

The alcohols can, as already shown (p. 315), be divided into primary, secondary, and tertiary derivatives; the same classification may also be carried out with the glycols, but in addition we can also obtain glycols which have simultaneously the characteristics of two of these groups. This is evident from an examination of the following constitutional formulae:

Primary.

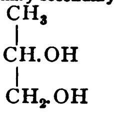
Ethylene glycol



$$\begin{array}{l} CH_2.OH \\ | \\ CH_2.OH \end{array}$$

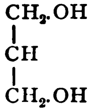
Primary-secondary.

Propylene glycol



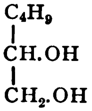
$$\begin{array}{l} CH_3 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

Trimethylene glycol



$$\begin{array}{l} CH_2.OH \\ | \\ CH \\ | \\ CH_2.OH \end{array}$$

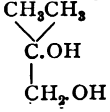
Hexylene glycol



$$\begin{array}{l} C_4H_9 \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

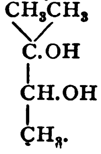
Primary-tertiary.

Isobutylene glycol



$$\begin{array}{c} CH_3CH_3 \\ \diagdown\diagup \\ C.OH \\ | \\ CH_2.OH \end{array}$$

Secondary-tertiary.



$$\begin{array}{c} CH_3CH_3 \\ \diagdown\diagup \\ C.OH \\ | \\ CH.OH \\ | \\ CH_3. \end{array}$$

The boiling point of the members of the glycol series here mentioned does not rise regularly, as usual, with the increase in the number of carbon atoms, as the glycols given do not form a real homologous series, some being primary, others secondary, and others primary-secondary, &c.

Ethylene, C_2H_4.

This substance, also known as *olefiant gas*, has already been mentioned (p. 90). It is formed in the dry distillation of coal and various organic bodies, but is best prepared by the action of hot sulphuric acid on alcohol; a mixture of 1 part of alcohol and 4 parts of sulphuric acid is heated in a flask with enough sand to form a pasty mass. The alcohol loses the elements of one molecule of water, and ethylene is formed. The chief physical properties of ethylene have already been mentioned. It combines directly with 2 atoms of chlorine, and with hydrochloric and hydriodic acids: with chlorine it forms ethylene dichloride; with the hydracids it forms ethyl chloride, bromide, and iodide. It is absorbed by concentrated sulphuric acid, forming ethyl-sulphuric acid (p. 329).

Ethylene Dichloride, $C_2H_4Cl_2$.—Olefiant gas derives its name from its power of forming an oil when brought into contact with chlorine. On mixing these gases, drops are formed; and when collected, washed, and distilled, they yield the pure dichloride. This body boils at 85°, and is insoluble in water, but dissolves in alcohol and ether. It is rapidly attacked by chlorine, and substitution-products are formed, in which one, two, three, and lastly four, atoms of hydrogen are replaced by chlorine. Thus we have:

	Boiling Point.
$C_2H_4Cl_2$	83°·5
$C_2H_3Cl_3$	115°
$C_2H_2Cl_4$	147°
C_2HCl_5	158°
C_2Cl_6	182°

Glycol, or *Ethylene Alcohol*, $C_2H_4(OH)_2$.—This substance is obtained by the action of ethylene dibromide upon silver acetate, silver bromide and glycol diacetate being formed:

$$\overset{\text{Ethylene Dibromide}}{C_2H_4Br_2} + \overset{\text{Silver Acetate}}{2C_2H_3O.OAg} = \overset{\text{Silver Bromide}}{2AgBr} + \overset{\text{Glycol Diacetate.}}{C_2H_4(OC_2H_3O)_2}.$$

The pure glycol is obtained from the acetate by acting on it with baryta; it is, however, more easily prepared by heating the dibromide with a solution of potassium carbonate:

$$C_2H_4Br_2 + CO(OK)_2 = C_2H_4(OH)_2 + 2KBr + CO_2.$$

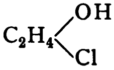
Glycol is a colourless, inodorous, and sweetish tasting, thick liquid; its specific gravity at 0° is 1·125, it boils at $197^{\circ}{\cdot}5$, and is soluble in all proportions in alcohol and water. When exposed to air in contact with water and platinum black, it absorbs oxygen rapidly, and is converted into glycollic acid:

$$CH_2(OH).CH_2(OH) + O_2 = H_2O + CH_2(OH).CO(OH).$$

On treatment with hot nitric acid glycol undergoes further oxidation forming oxalic acid:

$$CH_2(OH).CH_2(OH) + 2O_2 = CO(OH).CO(OH) + 2H_2O.$$

From these reactions it appears that glycollic and oxalic acids stand to glycol as acetic acid does to ethyl alcohol. A substance having the composition $C_2H_2O_2$, *i.e.* CHO.CHO, and called *glyoxal*, stands in the relation of an aldehyde to glycol. Glycol acts like alcohol in other respects; the typical hydrogen can be replaced by sodium, forming compounds analogous to sodium ethylate: it also forms a compound with sulphuric acid, called *glyco-sulphuric acid*.

As already mentioned, glycol differs from alcohol inasmuch as it yields "mixed" derivatives. Thus the first product of the reaction of hydrochloric acid on glycol is *ethylene chlorhydrin*  $C_2H_4\begin{cases}OH\\Cl\end{cases}$, also obtained by the addition of hypochlorous acid to ethylene. By the further action of hydrochloric acid, a second replacement of the same kind occurs, and ethylene chloride is formed.

$$\overset{\text{(1) Glycol.}}{CH_2(OH).CH_2(OH)};\quad \overset{\text{(2) Glycol Chlorhydrin.}}{CH_2Cl.CH_2(OH)};\quad \overset{\text{(3) Ethylene Chloride.}}{CH_2Cl.CH_2Cl.}$$

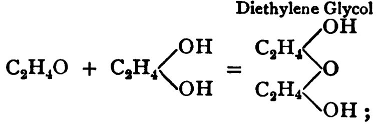
There are also two acetates of glycol known, the *mono-acetate* and *di-acetate:*

$CH_2(OH).CH_2(O.C_2H_3O)$ and $CH_2(O.C_2H_3O).CH_2(O.C_2H_3O)$.

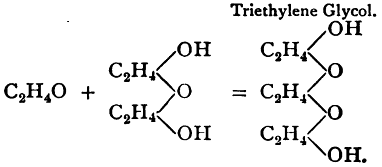
Two ethyl compounds exist, mono-ethyl glycol and di-ethyl glycol: this latter body is isomeric with acetal (p. 358).

Ethylene Oxide, C_2H_4O.—This substance is prepared by the action of potash on ethylene chlorhydrin, which loses a molecule of hydrochloric acid and forms ethylene oxide. It is a volatile colourless liquid, boiling at 13°·5, soluble in all proportions in water. It does not, like the isomeric aldehyde, form a crystalline compound with ammonia, but combines readily with hydrogen, chlorine, acids, &c. Alcohol, C_2H_6O, is formed by the direct union of ethylene oxide with H_2; and on oxidation glycollic acid is produced.

Ethylene oxide also unites directly with one molecule of water, forming glycol, and also with glycol to form polyethylene glycols:

(1) 

$$C_2H_4O + C_2H_4\begin{cases}OH\\OH\end{cases} = \begin{array}{l}C_2H_4\begin{cases}OH\\ \end{cases}\\ \qquad >O\\ C_2H_4\begin{cases} \\OH;\end{cases}\end{array}$$

(2) 

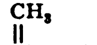
$$C_2H_4O + \begin{array}{l}C_2H_4\begin{cases}OH\\ \end{cases}\\ \qquad >O\\ C_2H_4\begin{cases} \\OH\end{cases}\end{array} = \begin{array}{l}C_2H_4\begin{cases}OH\\ \end{cases}\\ \qquad >O\\ C_2H_4\\ \qquad >O\\ C_2H_4\begin{cases} \\OH.\end{cases}\end{array}$$

Many compounds of ethylene with the elements of the nitrogen group are known. The dyad ethylene replaces two atoms of hydrogen in two molecules of ammonia; and thus primary, secondary, and tertiary *diamines* and ammonium compounds are formed closely analogous to the compounds of ethyl. The ethylene diamines are volatile bases obtained by acting with ammonia on ethylene dibromide. Similar compounds in the phosphorus and arsenic series are also known.

Choline, or *Hydroxyethyltrimethylammonium hydroxide*, $N(C_2H_4OH)(CH_3)_3OH$, is a strong base first prepared from the bile, and afterwards found in the brain and in yolk of eggs, but it does not exist as such in these substances, being the result of the decomposition of more complicated bodies. It can be artificially prepared by heating ethylene oxide with trimethylamine and water:

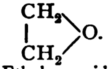
$$C_2H_4O + N(CH_3)_3 + H_2O = CH_2(OH).CH_2.N(CH_3)_3OH.$$

Ethidene Compounds. Acetaldehyde is isomeric with ethylene oxide, the constitution of the two compounds being represented by the formulæ:



$$\begin{array}{l} CH_3 \\ \| \\ CH = O \end{array}$$

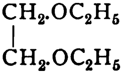
Acetaldehyde.



Ethylene oxide.

Acetaldehyde may therefore be regarded as the oxide of the radical $CH_3.CH=$, isomeric with ethylene. It is not known in the free state, but occurs in combination with other radicals such as chlorine, OC_2H_5, &c., these compounds being known as ethidene derivatives.

Ethidene chloride, $CH_3.CHCl_2$, is obtained by the action of phosphorus pentachloride on aldehyde or of chlorine on ethane or ethyl chloride. It is a liquid boiling at 58°.

Acetal, $CH_3.CH(OC_2H_5)_2$, is formed as a by-product in the preparation of aldehyde from alcohol, and by the action of sodium ethylate on ethidene bromide. It is a colourless, pleasant-smelling liquid, which boils at 104°, whilst the isomeric *ethylene diethyl ether*,  $\begin{array}{l} CH_2.OC_2H_5 \\ | \\ CH_2.OC_2H_5 \end{array}$, boils at 123°·5.

Propylene, $CH_3.CH{:}CH_2$, is prepared by heating secondary propyl iodide with alcoholic potash, and is a gas resembling ethylene; its *dibromide* boils at 141°·6, and its *glycol* at 188°.

DIVALENT ACIDS, RESULTING FROM THE OXIDATION OF THE PRIMARY GLYCOLS.

There are two series of these acids: the first derived by the replacement of 2 atoms of hydrogen in the corresponding diatomic alcohol by 1 atom of oxygen, and the second by the replacement of 4 atoms of the hydrogen by 2 atoms of oxygen. The first of these groups of acids may be termed the *Lactic Acid Series*, and the second the *Oxalic Acid Series*,—from the acid best known in each series; the members of the first series are also known as the *hydroxy-acids*, as they may be regarded as fatty acids in which one atom of hydrogen is replaced by hydroxyl. The relation of glycol to glycollic acid, the first of the lactic acids, and to oxalic acid, serving as a type of the general relations, is seen in the following:

Glycol.	Glycollic Acid.	Oxalic Acid.
$\left\{\begin{array}{l}CH_2OH\\CH_2OH\end{array}\right.;$	$\left\{\begin{array}{l}CH_2OH\\CO.OH\end{array}\right.;$	$\left\{\begin{array}{l}CO.OH\\CO.OH\end{array}\right..$

The following is a list of the more important of these acids:

Lactic Acid Series (*Monobasic*).

General formula, $C_nH_{2n}O_3$.

Name of Acid.	Formula.
Carbonic Acid (Hydrate)	CH_2O_3.
Glycollic	$C_2H_4O_3$.
Lactic	$C_3H_6O_3$.
Hydroxybutyric	$C_4H_8O_3$.
Hydroxyvaleric	$C_5H_{10}O_3$.
Leucic	$C_6H_{12}O_3$.

Oxalic Series of Acids (*Dibasic*).

General formula, $C_nH_{2n-2}O_4$.

Name of Acid.	Formula.
Oxalic	$C_2H_2O_4$.
Malonic	$C_3H_4O_4$.
Succinic	$C_4H_6O_4$.
Pyrotartaric	$C_5H_8O_4$.
Adipic	$C_6H_{10}O_4$.
Pimelic	$C_7H_{12}O_4$.
Suberic	$C_8H_{14}O_4$.
Azelaic	$C_9H_{16}O_4$.
Sebacic	$C_{10}H_{18}O_4$.
Brassylic	$C_{11}H_{20}O_4$.
Rocellic	$C_{17}H_{32}O_4$.

The initial member of the first series, *carbonic acid*, which has already been described in the inorganic portion of the book may also be looked upon as *hydroxyformic acid:*

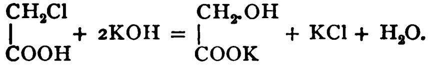
$H.CO.OH$	$HO.CO.OH$
Formic Acid.	Carbonic Acid.

It differs, however, from the higher members of the series in containing two atoms of replaceable hydrogen. This is accounted for by the fact that in this acid both hydroxyl groups are directly connected with the carbonyl, which is not the case in any of the others. Hence two sets of carbonates exist:

Normal sodium carbonate	$CO(ONa)_2$.
Hydrogen sodium carbonate	$CO(OH)ONa$.

The other acids of the first series are *monobasic*, containing only one carboxyl group (p. 314) while those of the second series are *dibasic*, or contain two such groups.

The acids of the first series contain the groups characteristic of both alcohols and acids, and as would be expected they show the properties of both series of compounds. They may be obtained by the action of alkalis on the halogen substituted acids: thus monochloracetic acid yields glycollic acid:



$$\begin{array}{l}CH_2Cl\\ |\\ COOH\end{array} + 2KOH = \begin{array}{l}CH_2.OH\\ |\\ COOK\end{array} + KCl + H_2O.$$

On the other hand, hydrobromic acid converts glycollic acid into monobromacetic acid.

Glycollic Acid, or Hydroxyacetic Acid, $CH_2(OH).COOH$, is prepared as above mentioned by the action of water or alkalis on chloracetic acid, and is also formed when alcohol is oxidized with nitric acid. It forms colourless crystals, very soluble in water, and occurs in unripe grapes, and in the leaves of the wild vine.

Lactic Acid, or *a-Hydroxypropionic Acid*, $C_3H_6O_3$.

Two different acids may be obtained from propionic acid, $CH_3.CH_2.COOH$, by substituting one atom of hydrogen by hydroxyl, viz.:

(1)	(2)
$CH_3.CH(OH).COOH$	$CH_2(OH).CH_2.COOH.$
α-Hydroxypropionic Acid or Lactic Acid.	β-Hydroxypropionic Acid, or Ethylenelactic Acid.

In order to distinguish these and similar substitution-compounds it is usual to give the prefix α to those in which the substituted radical is combined with the carbon atom adjacent to the carboxyl group; if the radical is combined with the carbon atom next but one to the carboxyl group, the prefix β is employed, if next but two γ, and so on. Thus a compound of the formula $CH_3.CHBr.CH_2.COOH$ is β-bromobutyric acid, whilst another of the formula $CH_2Br.CH_2.CH.OH.COOH$ would be β- hydroxy- δ- bromobutyric acid.

The above isomeric acids in this way become *α*- and *β*-hydroxypropionic acid. The first of these is by far the most important, and has long been known, as *lactic acid* or sometimes as *fermentation lactic acid.* It is contained in sour milk, and is prepared from sugar by a peculiar process known as the lactic fermentation, which is described more fully in the chapter on fermentation. It may be also artificially prepared as follows:

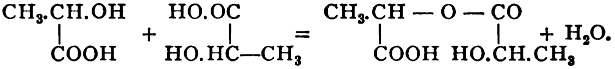
(1) By the oxidation of propylene glycol, $CH_3.CH(OH).CH_2.OH$.

(2) By the action of alkalis on *α*-chloropropionic acid, $CH_3.CHCl.COOH$.

(3) By allowing aldehyde, hydrocyanic acid, and hydrochloric acid to remain together for several days:

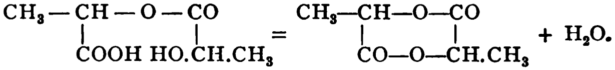
$$CH_3.CHO + HCN + HCl + 2H_2O = CH_3.CH(OH).COOH + NH_4Cl.$$

Lactic acid is an inodorous syrupy liquid of specific gravity 1·215, has a pleasant acid taste, and cannot be distilled unchanged: like other acids of this group it is simultaneously an acid and an alcohol, and on heating two molecules combine together, the one acting as an alcohol and the other as an acid:



$$\begin{array}{c}CH_3.CH.OH\\ |\\ COOH\end{array} + \begin{array}{c}HO.OC\\ |\\ HO.HC—CH_3\end{array} = \begin{array}{cc}CH_3.CH — O — & CO\\ | & |\\ COOH & HO.CH.CH_3\end{array} + H_2O.$$

This compound, known as *lactolactic acid*, is at the same time an alcohol, an acid, and an ethereal salt. On further heating it loses another molecule of water, thus



$$\begin{array}{cc}CH_3 — CH — O — & CO\\ | & |\\ COOH & HO.CH.CH_3\end{array} = \begin{array}{cc}CH_3—CH—O— & CO\\ | & |\\ CO—O— & CH.CH_3\end{array} + H_2O.$$

forming *lactide*, which is a double ethereal salt.

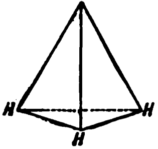
Another interesting series of reactions by which the double character of these acids is shown is the following: when lactic acid is heated with alcohol it is converted into the neutral compound *ethyl lactate*, $CH_3.CH(OH).COOC_2H_5$. Sodium acts on this compound in the same manner as on an alcohol, replacing the hydrogen atom of the hydroxyl group with formation of $CH_3.CH(ONa).COOC_2H_5$, and this by the action of ethyl iodide, C_2H_5I, yields *diethyl lactate*, $CH_3.CH(OC_2H_5).COOC_2H_5$. On boiling the latter with potash and acidifying, we obtain *ethyl lactic acid*, $CH_3\,CH(OC_2H_5)COOH$, which is as strong an acid as lactic acid itself.

Of its salts the most important are *zinc lactate*, $(C_3H_5O_3)_2Zn$, which crystallizes well and is sparingly soluble in water, and *ferrous lactate* $(C_3H_5O_3)_2Fe + 3H_2O$, which is employed in medicine.

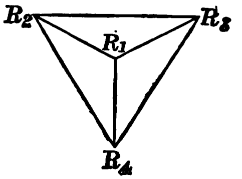
Paralactic acid or sarcolactic acid is contained in the juice of flesh, and is only distinguished from the ordinary lactic acid by the fact that if a ray of polarized light be passed through it, the plane of polarization is rotated to the right, whereas the ordinary acid has no such effect. An acid has also recently been obtained which resembles both the foregoing acids in general properties, but rotates the plane of polarization to the left, as much as paralactic acid does to the right. The chemical properties of all three agree with the constitutional formula $CH_3.CH(OH).COOH$, but this gives no explanation of their different optical properties.

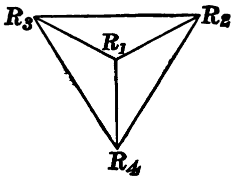
To account for this difference, a very ingenious hypothesis has been brought forward by Le Bel and Van't Hoff, which takes into account the relative positions of the atoms in space instead of only representing them in two dimensions on a plane, such as a piece of paper.

In the simplest case, when the carbon atom is combined with four monovalent atoms, it is assumed that these are uniformly distributed in space, and therefore occupy the same position on the surface of a sphere of which the carbon atom occupies the centre, as the corners of a regular tetrahedron inscribed in that sphere; this may be graphically represented by placing the atoms at the corners of a regular tetrahedron, the carbon atom being situated at the centre. Methane or marsh-gas then receives the formula :



Now if instead of having the same atoms combined with the carbon atom, we have four different atoms or groups, R_1, R_2, R_3, R_4, we can get two different arrangements, as shown in the following formulæ, supposing that the observer is looking down on the tetrahedra from above.





These two "configurations" are not superposable, but they have the same relation to one another as an object has to its image in a plane mirror.

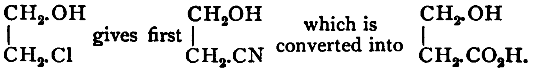
Now in lactic acid we have a compound containing four different atoms or groups in combination with one carbon atom, viz., H, OH, CH_3, COOH, and by substituting these for R_1, R_2, R_3, R_4, in the above formulæ, we should obtain two configurations for lactic acid. These are assumed by the hypothesis to represent the two optically active lactic acids, whilst the inactive compound is supposed to be a mixture of equal quantities of the two active varieties, which therefore neutralize one another in their action on polarized light.

If the hypothesis is correct, all optically active compounds should contain a carbon atom in combination with four other unlike atoms or groups, or in other words should contain an "asymmetric" carbon atom, and as a matter of fact no optically active carbon compound has yet been studied which does not fulfil this condition. In certain cases, too, the inactive isomeride has been actually separated into its two active constituents (see Racemic Acid).

Ethylene lactic acid is formed from β-iodopropionic acid, as follows:

$$CH_2I.CH_2.CO_2H + AgOH = CH_2(OH).CH_2.CO_2H + AgI.$$

Also by the action of potassium cyanide and hydrochloric acid on ethylene chlorhydrin :—hence the name ethylene lactic acid.



$$\begin{array}{l}CH_2.OH\\ |\\ CH_2.Cl\end{array} \text{ gives first } \begin{array}{l}CH_2OH\\ |\\ CH_2.CN\end{array} \begin{array}{c}\text{which is}\\ \text{converted into}\end{array} \begin{array}{l}CH_2.OH\\ |\\ CH_2.CO_2H.\end{array}$$

Hydroxybutyric acids, $C_4H_7(OH).COOH$.—Three hydroxy-derivatives of butyric acid exist, viz. :

$CH_3.CH_2.CH(OH).COOH$
α-Hydroxybutyric Acid.

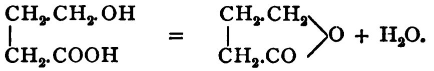
$CH_3.CH(OH).CH_2.COOH$
β-Hydroxybutyric Acid.

$CH_2(OH).CH_2.CH_2.COOH.$
γ-Hydroxybutyric Acid.

The α-compound corresponds to lactic acid in its properties. The second acid, and all β-hydroxy-acids readily lose water on heating, and are converted into unsaturated acids ; thus β-hydroxybutyric acid yields crotonic acid :

$$CH_3.CH(OH).CH_2.COOH = CH_3.CH{=}CH.CO_2H + H_2O.$$

The γ-hydroxy-acids also lose water on heating, but in quite a different manner, a peculiar anhydride being formed ; *e.g.*



$$\begin{array}{l}CH_2.CH_2.OH\\ |\\ CH_2.COOH\end{array} = \begin{array}{l}CH_2.CH_2\\ |\\ CH_2.CO\end{array}\!\!>O + H_2O.$$

These anhydrides are known by the general name of *lactones*.

The amido-substitution products of the fatty acids are also an important series of compounds, occurring frequently as decomposition products of albuminoid compounds.

Glycocoll or *Amidoacetic acid*, $CH_2(NH_2).COOH$, stands in close relation to glycollic acid, being obtained from chloracetic acid by the action of ammonia. It is a sweet tasting substance, and occurs in the gall and urine of graminivorous animals ; it is simultaneously a base and an acid, and forms salts with acids and with metals.

When hydrochloric acid gas is passed into its alcoholic solution it yields the *hydrochloride of ethyl amidoacetate*, $CH_2(NH_3Cl)CO_2C_2H_5$. By the action of sodium nitrite this forms a compound known as *ethyl diazoacetate*, $CHN_2.CO_2C_2H_5$, which is closely allied to the aromatic diazo-compounds subsequently described. This substance is a yellow liquid and is converted by caustic potash into a substance of complicated constitution known as *triazoacetic acid* $(C_3H_3N_6)_3(COOH)_3$, which crystallizes in deep orange coloured tablets and is decomposed on heating with dilute sulphuric acid into oxalic acid and hydrazine sulphate (p. 75).

Alanine or *a-Amidopropionic acid*, $CH_3.CH(NH_2).COOH$, corresponds to lactic acid, into which it is converted by the action of nitrous acid. *Leucine* or *Amidocaproic acid*, $C_5H_{10}(NH_2).COOH$, occurs in the brain, lungs and liver, and is formed in large quantities in certain illnesses, and in the decomposition products of albuminoids.

Oxalic Acid, $C_2H_2O_4$.

Oxalic acid is met with in the juice of many plants in the form of a potassium or calcium salt. It is formed in a great variety of ways, chiefly by the oxidation of different organic bodies. Oxalic acid can be prepared synthetically by heating carbon dioxide and sodium together to the boiling point of mercury :

$$2CO_2 + 2Na = C_2O_4Na_2;$$

also by heating the formate of an alkali metal:

$$\begin{matrix} H.CO.OK \\ H.CO.OK \end{matrix} = H_2 + \begin{matrix} CO.OK \\ | \\ CO.OK \end{matrix}$$

The best way of preparing pure oxalic acid on a small scale is by acting upon sugar with nitric acid: it was formerly manufactured in this way, but at present it is prepared in very large quantities by the action of caustic potash on sawdust. Crude potassium oxalate is thus formed, and from this a pure oxalic acid is obtained by precipitating the insoluble calcium oxalate, and decomposing this by sulphuric acid. Oxalic acid can also be obtained by the direct oxidation of glycollic acid.

Oxalic acid crystallizes in prisms which possess the composition $C_2H_2O_4 + 2H_2O$: these crystals lose their water of crystallization at 100°, or in a vacuum over sulphuric acid. When heated to about 160° oxalic acid rapidly decomposes, forming carbon dioxide, carbon monoxide, and formic acid, whilst a small quantity of oxalic acid sublimes undecomposed. Heated with sulphuric acid, oxalic acid is decomposed into water and equal volumes of carbon monoxide and carbon dioxide gases (p. 86). Oxalic acid is a dibasic acid, and forms two classes of salts called normal oxalates and acid oxalates. Another series of salts is also known, the members of which may be regarded as compounds of the acid salts with oxalic acid, and are termed *quadroxalates.* The oxalates of the alkali-metals are all soluble in water; the oxalates of the other metals are generally insoluble. The potassium oxalates are:

$C_2K_2O_4 + H_2O$ . . . . Potassium oxalate (normal oxalate).
$C_2HKO_4 + H_2O$ . . . Hydrogen potassium oxalate (binoxalate).
$C_2HKO_4 + C_2H_2O_4 + 2H_2O$ Potassium quadroxalate.

Calcium oxalate is a very insoluble salt, and is the form in which this metal is obtained for quantitative estimation. Methyl and ethyl oxalates are obtained by distilling the respective alcohols with oxalic acid: the first melts at 51° and boils at 162°, and the second boils at 186°; they have the composition

$$CO(OCH_3).CO(OCH_3). \qquad CO(OC_2H_5).CO(OC_2H_5).$$

Amides of Oxalic Acid.—By heating neutral ammonium oxalate, a white powder called *Oxamide* is left:

$$\overset{\text{Ammonium Oxalate}}{\begin{cases} CO_2NH_4 \\ CO_2NH_4 \end{cases}} = \overset{\text{Oxamide.}}{\begin{cases} CONH_2 \\ CONH_2 \end{cases}} + 2H_2O.$$

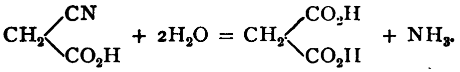
Oxamide, $CO(NH_2).CO(NH_2)$, may be considered as two molecules of ammonia, in which two atoms of hydrogen are replaced by C_2O_2. By heating hydrogen ammonium oxalate, a substance called *Oxamic Acid* is obtained, having the formula, $CO(OH).CO(NH_2)$.

Malonic Acid, $C_3H_4O_4$,

is formed by the oxidation of malic acid (p. 368). It is likewise obtained synthetically by the action of potash upon ethyl cyanacetate, thus:

$$\overset{\text{Ethyl Cyanacetate.}}{(CN)CH_2.CO.OC_2H_5} + 3H_2O = \overset{\text{Malonic Acid.}}{CO_2H.CH_2.CO_2H} + \overset{\text{Alcohol.}}{C_2H_6O} + NH_3$$

and also by acting on cyanacetic acid with alkalis or acids :



$$CH_2\begin{cases}CN\\CO_2H\end{cases} + 2H_2O = CH_2\begin{cases}CO_2H\\CO_2H\end{cases} + NH_3.$$

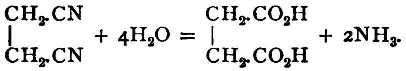
Ethyl malonate $CH_2(CO_2C_2H_5)_2$ is a pleasant smelling liquid which boils at 195°, and is largely used in organic synthesis.

Succinic Acid, $C_4H_6O_4$.

This acid is obtained by the distillation of amber; it occurs in amber, wormwood, in certain resins, and in small quantities in various animal juices, and is produced by the fermentation of sugar. It can be artificially prepared :

(1) By the action of hydriodic acid upon malic and tartaric acids.

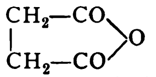
(2) By acting on ethylene dicyanide with potash :



$$\begin{array}{l}CH_2.CN\\|\\CH_2.CN\end{array} + 4H_2O = \begin{array}{l}CH_2.CO_2H\\|\\CH_2.CO_2H\end{array} + 2NH_3.$$

(3) By the action of nitric acid on butyric acid :

$$CH_3.CH_2.CH_2.CO_2H + 3O = H_2O + CO_2H.CH_2.CH_2.CO_2H.$$

Succinic acid forms large colourless crystals, which melt at 180°, and begin to boil at 235°, the vapour decomposing into succinic anhydride and water. It forms a chloride, $C_2H_4(C_2O_2Cl_2)$, as well as an anhydride  $\begin{array}{l}CH_2—CO\\|\\CH_2—CO\end{array}\!\!>O$ when heated with phosphorus pentachloride. Bromine substitution products are also known, viz., *monobromo-succinic acid*, $C_4H_5BrO_4$, and *dibromo-succinic acid*, $C_4H_4Br_2O_4$: these acids when treated with water and silver oxide are respectively converted into malic and tartaric acids. Succinic acid is dibasic, and forms two classes of salts : the salts of the alkali-metals are soluble, and these form an insoluble brown precipitate with ferric salts.

The ammonia derivatives of this acid are :

Succinamide, $C_2H_4\left\langle\begin{matrix}CO.NH_2\\CO.NH_2\end{matrix}\right.$, and *Succinimide*, $C_2H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle NH$.

Isosuccinic Acid.—This substance, which is isomeric with succinic acid, is obtained by the action of potash on cyanopropionic acid:

$$CH_3.CH(CN).CO_2H + 2H_2O = CH_3.CH : (CO_2H)_2 + NH_3.$$

Isosuccinic acid melts at 129°·5, and loses CO_2 on further heating forming propionic acid; it may thus be readily distinguished from its isomeride. It is derived from ethidene, as succinic acid is from ethylene.

For the special properties of the higher acids of this series the reader must consult a larger work on the subject.

LESSON XXXVI

VEGETABLE ACIDS AND THEIR DERIVATIVES

VERY intimately connected with succinic acid are two acids of much importance, viz., malic and tartaric acids.

Malic Acid, $C_4H_6O_5$.

This acid occurs in the juice of most fruits, especially in that of garden rhubarb and mountain-ash berries, from which it can be readily obtained. It can also be prepared by the substitution of hydroxyl for bromine in monobromosuccinic acid:

$$\underset{\text{Monobromosuccinic Acid.}}{C_2H_3Br\begin{cases}CO.OH\\CO.OH\end{cases}} + AgOH = \underset{\text{Malic Acid.}}{C_2H_3(OH)\begin{cases}CO.OH\\CO.OH\end{cases}} + AgBr.$$

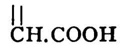
Malic acid is dibasic and crystallizes in indistinct very hygroscopic needles. The malates are soluble in water.

Asparagine, $C_2H_3(NH_2)\begin{cases}CO_2H\\CO.NH_2\end{cases}$, is a crystalline compound occurring in the juice of asparagus, which nitrous acid converts into malic acid.

FUMARIC AND MALEIC ACIDS.

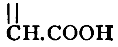
When malic acid is heated at 180°, it loses a molecule of water, forming a mixture of two isomeric acids of the formula $C_4H_4O_4$, termed *fumaric* and *maleic acid*. The former also occurs in the juices of certain plants. From their chemical properties both must have the constitution COOH.CH = CH.COOH. They nevertheless behave very differently in many respects; thus maleic acid readily yields an anhydride, whilst fumaric acid is very stable. For a long time no explanation could be given of the isomerism of these acids, but van't Hoff, by an extension of the views already given with regard to the asymmetric carbon atom (p. 363) has given a hypothesis which is accepted by the majority of chemists. For a detailed description of the hypothesis reference must be made to larger works: it is sufficient to state here that the explanation is arrived at by taking into account the relative positions of the atoms and groups in space. In maleic acid, the carboxyl groups are supposed to be close together, as it so readily yields an anhydride, and in the more stable fumaric acid the carboxyl groups are on opposite sides of the molecule; this is represented by the formulæ:

Fumaric Acid.



$$\begin{array}{ll} \text{COOH.CH} & \\ \quad\quad\; \| & \\ \quad\quad\; \text{CH.COOH} & \end{array}$$

Maleic Acid.



$$\begin{array}{l} \text{CH.COOH} \\ \| \\ \text{CH.COOH} \end{array}$$

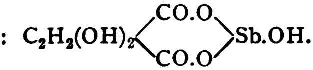
Such isomerides are possible in all cases where two carbon atoms are united by two combining units.

Tartaric acid, $C_4H_6O_6$.

Tartaric acid occurs in the juice of many fruits (grape, tamarind, &c.), and is deposited as the acid potassium salt during the fermentation of wine, the salt being known as *tartar* or *argol*. Free tartaric acid is obtained from the crude argol by boiling it with water and chalk, adding calcium chloride and decomposing the precipitated calcium tartrate with sulphuric acid. It crystallizes in large oblique monosymmetric prisms which dissolve easily in water. When heated to 180° it fuses and undergoes decomposition, evolving a peculiar odour of caramel. In presence of oxidizing agents, tartaric acid is converted into carbonic, formic, and oxalic acids; and when fused with caustic potash it forms acetic and oxalic acids. When tartaric acid is heated with hydriodic acid for several hours it is first reduced to malic, and afterwards to succinic acid, by losing first one and then a second atom of oxygen. Tartaric acid is a dibasic acid, containing two atoms of typical hydrogen which can be replaced by metals: hence there are two classes of alkaline tartrates; thus we have—

Hydrogen Potassium Tartrate (Cream of Tartar).
$$\begin{array}{l}CH(OH).CO.OK\\ |\\ CH(OH).CO.OH.\end{array}$$

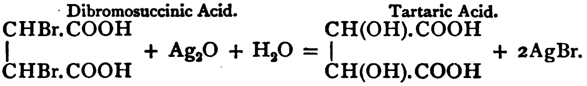
Normal Potassium Tartrate
$$\begin{array}{l}CH(OH).CO.OK\\ |\\ CH(OH).CO.OK.\end{array}$$

Tartaric acid forms with antimony a remarkable compound termed *Tartar Emetic.* It appears most probable that this is the potassium salt of an acid, having the following peculiar constitution:  $C_2H_2(OH)_2\begin{matrix}\diagup CO.O \diagdown\\ \diagdown CO.O \diagup\end{matrix}Sb.OH$. This substance is obtained by boiling a solution of cream of tartar with antimony trioxide; the oxide dissolves, and, on cooling, tartar emetic is deposited in crystals. This salt is much used in medicine, but acts as a violent poison when taken in quantity. Tartaric acid and citric acid are largely used by the calico-printer to act as a discharge or solvent for the mordant, thus giving white spots on a coloured ground.

Ordinary tartaric acid has the power of rotating the plane of polarization of light to the right. Several isomeric modifications, however, exist, which though closely allied chemically, differ considerably in their physical properties. Laevotartaric acid rotates the plane of polarization to the left to the same extent as ordinary or dextrotartaric acid rotates it to the right. Two inactive modifications termed *racemic* and *mesotartaric acid* are also known; the first has been resolved into equal parts of dextro- and laevotartaric acid, and is also obtained when solutions of those two acids are mixed, but mesotartaric acid cannot be resolved into two constituents.

The explanation of this isomerism is similar to that already given for lactic acid (p. 363). It will be seen from an examination of the constitutional formula of tartaric acid that it contains *two* asymmetric carbon atoms. In dextrotartaric acid the configuration of the group around each asymmetric carbon is such that both cause a rotation of the plane of polarization to the right, in laevotartaric acid both cause rotation to the left, whilst in mesotartaric the configuration around one asymmetric carbon is the reverse of that around the other, and the compound is therefore inactive. Racemic acid is, as already shown, a combination of equal quantities of the dextro- and laevo- acids.

The inactive mesotartaric acid is obtained by the action of silver oxide on dibromosuccinic acid, both atoms of bromine being replaced by hydroxyl :

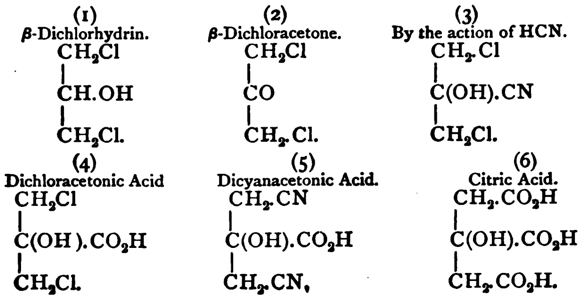


$$\underset{\text{Dibromosuccinic Acid.}}{\begin{array}{l}\text{CHBr.COOH}\\ |\\ \text{CHBr.COOH}\end{array}} + Ag_2O + H_2O = \underset{\text{Tartaric Acid.}}{\begin{array}{l}\text{CH(OH).COOH}\\ |\\ \text{CH(OH).COOH}\end{array}} + 2AgBr.$$

The mesotartaric acid is converted into racemic acid by heating to 175°.

Citric Acid, $C_6H_8O_7$.

This tribasic acid is found in the juice of the lemon, and occurs in many other fruits, together with malic acid. Citric acid is obtained from these sources and crystallizes in large colourless crystals, which dissolve very easily in water. It has also been prepared synthetically from glycerol by the following steps :—



$$\begin{array}{ccc}
\begin{array}{c}(1)\\ \beta\text{-Dichlorhydrin.}\\ \begin{array}{l}CH_2Cl\\ |\\ CH.OH\\ |\\ CH_2Cl.\end{array}\end{array} &
\begin{array}{c}(2)\\ \beta\text{-Dichloracetone.}\\ \begin{array}{l}CH_2Cl\\ |\\ CO\\ |\\ CH_2.Cl.\end{array}\end{array} &
\begin{array}{c}(3)\\ \text{By the action of HCN.}\\ \begin{array}{l}CH_2.Cl\\ |\\ C(OH).CN\\ |\\ CH_2Cl.\end{array}\end{array}\\
\begin{array}{c}(4)\\ \text{Dichloracetonic Acid}\\ \begin{array}{l}CH_2Cl\\ |\\ C(OH).CO_2H\\ |\\ CH_2Cl.\end{array}\end{array} &
\begin{array}{c}(5)\\ \text{Dicyanacetonic Acid.}\\ \begin{array}{l}CH_2.CN\\ |\\ C(OH).CO_2H\\ |\\ CH_2.CN,\end{array}\end{array} &
\begin{array}{c}(6)\\ \text{Citric Acid.}\\ \begin{array}{l}CH_2.CO_2H\\ |\\ C(OH).CO_2H\\ |\\ CH_2.CO_2H.\end{array}\end{array}
\end{array}$$

heated to 180° it fuses and undergoes decomposition, evolving a peculiar odour of caramel. In presence of oxidizing agents, tartaric acid is converted into carbonic, formic, and oxalic acids; and when fused with caustic potash it forms acetic and oxalic acids. When tartaric acid is heated with hydriodic acid for several hours it is first reduced to malic, and afterwards to succinic acid, by losing first one and then a second atom of oxygen. Tartaric acid is a dibasic acid, containing two atoms of typical hydrogen which can be replaced by metals: hence there are two classes of alkaline tartrates; thus we have—

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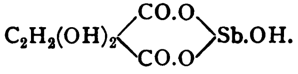
Tartaric acid forms with antimony a remarkable compound termed *Tartar Emetic.* It appears most probable that this is the potassium salt of an acid, having the following peculiar constitution:  $C_2H_2(OH)_2\left\langle\begin{array}{c} CO.O \\ CO.O \end{array}\right\rangle Sb.OH.$ This substance is obtained by boiling a solution of cream of tartar with antimony trioxide; the oxide dissolves, and, on cooling, tartar emetic is deposited in crystals. This salt is much used in medicine, but acts as a violent poison when taken in quantity. Tartaric acid and citric acid are largely used by the calico-printer to act as a discharge or solvent for the mordant, thus giving white spots on a coloured ground.

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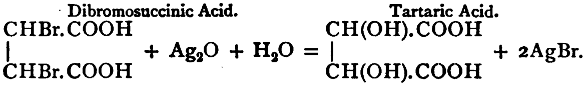

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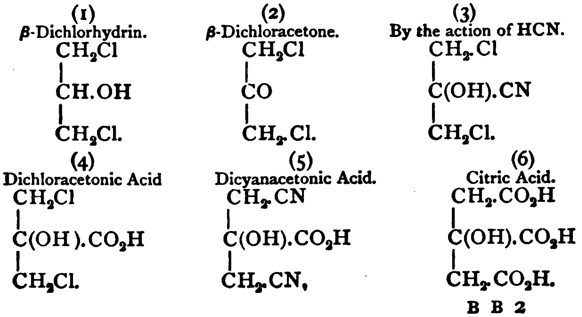


(1) β-Dichlorhydrin. $\begin{array}{l}CH_2Cl\\ |\\ CH.OH\\ |\\ CH_2Cl.\end{array}$

(2) β-Dichloracetone. $\begin{array}{l}CH_2Cl\\ |\\ CO\\ |\\ CH_2.Cl.\end{array}$

(3) By the action of HCN. $\begin{array}{l}CH_2.Cl\\ |\\ C(OH).CN\\ |\\ CH_2Cl.\end{array}$

(4) Dichloracetonic Acid $\begin{array}{l}CH_2Cl\\ |\\ C(OH).CO_2H\\ |\\ CH_2Cl.\end{array}$

(5) Dicyanacetonic Acid. $\begin{array}{l}CH_2.CN\\ |\\ C(OH).CO_2H\\ |\\ CH_2.CN,\end{array}$

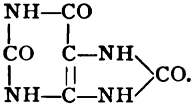
(6) Citric Acid. $\begin{array}{l}CH_2.CO_2H\\ |\\ C(OH).CO_2H\\ |\\ CH_2.CO_2H.\end{array}$

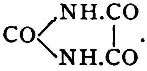
Three series of citrates exist, in which one, two, or three atoms of hydrogen are replaced by metal. The citrates of the alkali-metals are soluble, those of the alkaline-earth metals, of lead, and silver, are insoluble in water.

URIC ACID AND ITS DERIVATIVES.

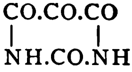
Uric Acid, $C_5H_4N_4O_3$.—This substance, found in the urine of birds, serpents, &c., is a dibasic acid and forms salts which are only slightly soluble in water : of these the lithium urates dissolve the most readily. Uric acid is best prepared from guano ; this is boiled with caustic soda, and on adding hydrochloric acid to the solution uric acid separates out as a white crystalline powder.

It has been obtained synthetically by a series of somewhat complicated reactions from urea and acetoacetic ether (*v.* chapter on Organic Synthesis), and a clear light has thus been thrown on its constitution, which is represented by the formula:



On oxidation it yields a number of interesting derivatives, which are combinations of urea with acid residues. Thus the compound obtained by the oxidation of uric acid with hot fairly concentrated, nitric acid, termed *parabanic acid*, is *oxalyl urea* 

$$\mathrm{CO}\left\langle\begin{array}{l}\mathrm{NH.CO}\\ \qquad\ \mid\\ \mathrm{NH.CO}\end{array}\right.$$

. Dilute nitric acid at 60—70° converts uric acid into *alloxan* or *mesoxalyl urea* 

$$\begin{array}{l}\mathrm{CO.CO.CO}\\ \mid\qquad\qquad\ \mid\\ \mathrm{NH.CO.NH}\end{array}$$

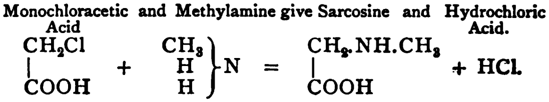
On evaporating uric acid carefully to dryness with nitric acid, a reddish residue is obtained, which becomes purple red when moistened with ammonia. This is the ammonium salt of an acid termed purpuric acid, and was formerly largely employed as a colouring matter under the name *murexide*. It forms crystals, which have a green metallic lustre, and the composition $C_8H_4(NH_4)N_5O_6$, and gives a beautiful purple solution with water, the colour changing to blue on addition of potash.

Xanthine, $C_5H_4N_4O_2$; *Sarcine*, $C_5H_4N_4O$, and *Guanine*, $C_5H_5N_5O$, are compounds occurring in the animal organism closely related to uric acid.

Creatine, $C_4H_9N_3O_2+H_2O$, occurs in small quantities in muscular tissue and urine, and is formed, like urea and uric acid, by the oxidation of the nitrogenous animal tissue. It crystallizes in bright colourless prisms, and in contact with baryta water decomposes into urea and sarcosine:

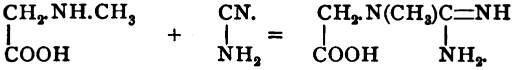
$$\underset{\text{Creatine}}{C_4H_9N_3O_2} + H_2O \overset{\text{yields}}{=} \underset{\text{Urea}}{CH_4N_2O} \overset{\text{and}}{+} \underset{\text{Sarcosine.}}{C_3H_7NO_2}.$$

Sarcosine can be artificially prepared by acting upon monochloracetic acid with methylamine: it is therefore methyl-glycocoll.



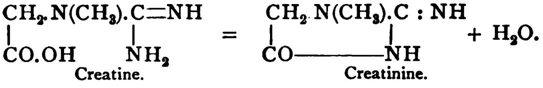
$$\begin{array}{ccccccc} \text{Monochloracetic Acid} & \text{and} & \text{Methylamine} & \text{give} & \text{Sarcosine} & \text{and} & \text{Hydrochloric Acid.} \\ \begin{array}{l} CH_2Cl \\ | \\ COOH \end{array} & + & \left.\begin{array}{l} CH_3 \\ H \\ H \end{array}\right\}N & = & \begin{array}{l} CH_2.NH.CH_3 \\ | \\ COOH \end{array} & + & HCl \end{array}$$

If sarcosine be heated with an alcoholic solution of cyanamide it reforms creatine.



$$\begin{array}{l} CH_2.NH.CH_3 \\ | \\ COOH \end{array} + \begin{array}{l} CN. \\ | \\ NH_2 \end{array} = \begin{array}{ll} CH_2.N(CH_3)C{=}NH & \\ | & \;\;| \\ COOH & \;\;NH_2. \end{array}$$

Creatinine is obtained by eliminating 1 molecule of water from creatine:



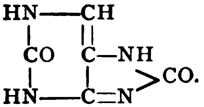
$$\underset{\text{Creatine.}}{\begin{array}{ll} CH_2.N(CH_3).C{=}NH & \\ | \qquad\qquad\quad | & \\ CO.OH \qquad NH_2 & \end{array}} = \underset{\text{Creatinine.}}{\begin{array}{l} CH_2.N(CH_3).C:NH \\ | \qquad\qquad\quad | \\ CO\text{———}NH \end{array}} + H_2O.$$

It also occurs in urine, and crystallizes in colourless prisms; its solution has an alkaline reaction, and it yields with acids a series of well crystallized salts.

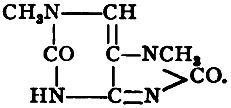
Theobromine, $C_7H_8N_4O_2$, a weak base contained in cacao-beans, is a white crystalline powder having a bitter taste. It can be artificially prepared from xanthine, by dissolving it in caustic soda and adding lead acetate, when lead xanthate, $C_5H_2PbN_4O_2$, is precipitated, and this, on heating with methyl iodide, yields dimethyl-xanthine or theobromine. If this latter body be again treated in a similar manner, methyl-theobromine or caffeine is obtained.

Caffeine or *Theine*, $C_7H_7(CH_3)N_4O_2$, is the active principle in coffee and tea ; it is also found in the leaves of the *Ilex paraguaensis*, a decoction of which is used in South America in place of tea, and also in *guarana*, a kind of chocolate made from the fruit of the *Paulinia sorbilis*. The quantity of caffeine contained in tea is about 2 per cent., whilst coffee contains 0·8 to 1 per cent., guarana 5 per cent., and Paraguay tea about 1·2 per cent.

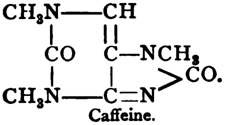
Xanthine, theobromine and caffeine possess a constitution similar in many respects to that of uric acid, as will be seen from the following formulæ :



Xanthine.



Theobromine.



Caffeine.

LESSON XXXVII

TRIAD ALCOHOLS AND THEIR DERIVATIVES

THE hydrocarbon radicals having the general formula C_nH_{2n-1} act, in accordance with the views already expressed (p. 279), as trivalent radicals yielding alcohols of which *glycerine* or *glycerol*, $C_3H_5(OH)_3$, is the best known.

The relation existing between the monad-, dyad-, and triad alcohols of the same carbon series is a very simple one, as is seen by the following comparison of the three-carbon series :

Propane	C_3H_8.
Propyl alcohol	C_3H_7OH.
Propylene alcohol or glycol	$C_3H_6(OH)_2$.
Propenyl alcohol or glycerol	$C_3H_5(OH)_3$.

The glycerols of the mono- and di-carbon series have not been prepared; that of the tri-carbon series is best known, and may be taken as the type: higher glycerols have also been prepared.

Glycerol, Glycerine, or *Propenyl Alcohol*, $C_3H_5(OH)_3$.—This substance is contained in most oils and fats, both vegetable and animal, which consist of glycerol salts of the higher members of the fatty acid series and of the oleic series: thus beef-suet or *stearin*, is glyceryl tristearate, or glycerol in which the 3 atoms of typical hydrogen have been replaced by 3 molecules of the radical of stearic acid $C_{18}H_{35}O$ (p. 344); whilst olive oil consists chiefly of propenyl trioleate. Glycerol is also produced in small quantities in the fermentation of sugar, and is formed from fats by the process of *saponification*, or treatment of the oil with caustic alkali, which decomposes the compound, forming an alkaline stearate (soap), and liberating the glycerol, which remains in solution when the soap is separated by throwing in common salt. In order to obtain pure glycerol, the fat may be decomposed by lead oxide; the glycerol remains in solution, and the lead soap or plaister is precipitated. Another and better method is to decompose the fats with high pressure steam, free stearic acid and glycerol being produced.

$$\overset{\text{Tristearin.}}{C_3H_5O_3(C_{18}H_{35}O)_3} + 3H_2O = \overset{\text{Glycerol.}}{C_3H_5(OH)_3} + \overset{\text{Stearic Acid.}}{3C_{18}H_{36}O_2}.$$

Glycerol is a colourless thick syrupy liquid, of specific gravity 1·27; it possesses a very sweet taste (whence its name), and is soluble in water and alcohol. It can be distilled in presence of aqueous vapour and in a vacuum, but it undergoes decomposition when heated in the air. When mixed with dilute nitric acid, glycerol undergoes oxidation and forms *glyceric acid*, $C_3H_6O_4$, by exchange of H_2 for O: this acid therefore stands to glycerol as acetic acid does to ethyl alcohol; glycerol, $CH_2(OH).CH(OH).CH_2(OH).$; glyceric acid, $CH_2(OH).CH(OH).CO_2H$. Glycerol is reduced by hydriodic acid to secondary propyl iodide.

Propenyl Nitrate, *Nitro-glycerol*, or *Nitro-glycerine*, $C_3H_5(NO_3)_3$, is prepared by acting on glycerol in the cold with a mixture of strong nitric and sulphuric acids.

This substance explodes violently on percussion, and has been used for blasting and other purposes under the name of Nobel's Blasting Oil, or Glonoin Oil. It is, however, extremely dangerous, and has caused many fatal accidents. It is absorbed in large quantities by a siliceous earth known as *kieselguhr*, and is then termed *Dynamite*, in which form it may be handled with comparative safety.

Heated with hydrochloric acid, glycerol forms compounds termed *Chlorhydrins*, by the replacement of 1, 2, or 3 hydroxyl groups (OH) by chlorine. Of each of the first two terms, *i.e.*, monochlorhydrin and dichlorhydrin, there are two isomerides (compare with primary and secondary propyl compounds); thus there is the *a-dichlorhydrin*, $CH_2(OH).CHCl.CH_2Cl$, and the *β-dichlorhydrin*, $CH_2Cl.CH(OH).CH_2Cl$.

Glycerol.	Chlorhydrin.	Dichlorhydrin.	Trichlorhydrin.
$C_3H_5(OH)_3$;	$C_3H_5(OH)_2Cl$;	$C_3H_5(OH)Cl_2$;	$C_3H_5Cl_3$.

Glycerol Ethers of the Fatty Acids.—The *acetins* are prepared by the action of strong acetic acid upon glycerol; they are three in number:

Mono-acetin.	Di-acetin.	Tri-acetin.
$C_3H_5(OH)_2(OC_2H_3O)$;	$C_3H_5(OH)(OC_2H_3O)_2$;	$C_3H_5(OC_2H_3O)_3$.

These substances, which resemble the fats in constitution, are obtained by acting upon glycerol with glacial acetic acid. They are thick oily liquids, only sparingly soluble in water, and boiling at a high temperature.

By the action of sodium ethylate upon mono-, di-, and trichlorhydrin, the three ethyl-propenyl ethers, or *ethylins*, have been prepared; these are:

Ethylin.	Diethylin.	Triethylin.
$C_3H_5.(OH)_2(OC_2H_5)$;	$C_3H_5(OH)(OC_2H_5)_2$;	$C_3H_5(OC_2H_5)_3$.

The Natural Fats and Oils.—The Stearic, Palmitic, and Oleic ethers of glycerol, or *Stearins*, *Palmitins*, *and*

Oleins, are of great importance, as forming the natural fats. The stearins may be prepared artificially by heating glycerol with stearic acid.

Monostearin. Distearin.

$$C_3H_5(OH)_2(OC_{18}H_{35}O)\ ;\ C_3H_5(OH)(O.C_{18}H_{35}O)_2\ ;$$

Tristearin.

$$C_3H_5(O.C_{18}H_{35}O)_3.$$

Tristearin can be obtained by melting beef or mutton suet, separating the fibrous matter by filtration and crystallizing the stearin from solution in hot ether. It forms bright white shining plates, insoluble in alcohol and water, but readily soluble in ether.

Corresponding propenyl ethers have been prepared with many of the other members of the series of fatty acids.

The fats cannot be distilled without decomposition, and, when heated, give rise to a powerfully smelling substance called *acrolein* (p. 379). The oils are divided into the drying and non-drying classes ; the former become dry and resinous on exposure to air from oxidation, whilst the others remain unaltered. The drying oils are generally glycerides of acids not belonging to the fatty acid series, though closely related to them (see p. 380) : such, for instance, is the acid of linseed oil, called linoleic acid, $C_{16}H_{28}O_2$. Oleic acid, $C_{18}H_{34}O_2$, another acid of this series, is found in almost all oils and fats, the compound of this acid with glycerol constituting the liquid portions of the fats.

Fatty bodies when boiled with alkali undergo the change termed *Saponification* (p. 375) ; the fat is decomposed into a fatty acid, which combines with the alkali, yielding a soap, and glycerol is liberated ; both pass into solution. The soap is then thrown out of solution by addition of common salt ; if soda be used as the alkali a hard soap is obtained ; if potash be employed, soft soap remains. The saponification of a fat corresponds exactly to the decomposition of an ethereal salt—or of an inorganic salt—by an alkali ; and indeed it is frequent to speak of the "saponification" of ethers, such as ethyl acetate, &c., although the salt formed has none of the familiar properties of a soap. The term *hydrolysis* is now however usually employed in such cases.

$$\underset{\text{Stearin.}}{C_3H_5.(O.C_{18}H_{35}O)_3} + 3KOH = \underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\text{Potassium stearate.}}{3C_{18}H_{35}O.OK.}$$

$$\underset{\text{Ethyl acetate.}}{C_2H_5.O.C_2H_3O} + KOH = \underset{\text{Ethyl alcohol.}}{C_2H_5.OH} + \underset{\text{Potassium acetate.}}{C_2H_3O.OK.}$$

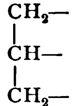
$$\underset{\text{Ferrous sulphate.}}{FeSO_4} + 2KOH = \underset{\text{Ferrous hydrate.}}{Fe(OH)_2} + \underset{\text{Potassium sulphate.}}{K_2SO_4.}$$

Lecithin, $C_{42}H_{84}NPO_9$, is a wax-like body found in the brain, nerves, and blood corpuscles. When boiled with an acid it is resolved into glyceryl—phosphoric acid, choline, and either stearic, palmitic, or oleic acid, or a mixture of these. The substance is therefore a mixture of choline and stearic, palmitic, or oleic acid derivatives of glycerol—phosphoric acid; that derived from stearic acid has the constitution:

$$C_3H_5\left\{\begin{array}{l} O.PO.(OH)OC_2H_4N(CH_3)_3OH. \\ O.C_{18}H_{35}O. \\ O.C_{18}H_{35}O. \end{array}\right.$$

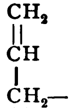
Allyl Compounds.

The trivalent radicals, C_nH_{2n-1}, can also act as monovalent radicals when two atoms of carbon are doubly linked. Hence the compounds of these radicals stand to the olefines in the same relation as the compounds of the monad radicals methyl, ethyl &c., do to the paraffins. They combine readily with bromine or hydrogen, and in this respect differ essentially from the compounds of the ethyl, ethenyl, and propenyl series. The best known of these monad radicals is *allyl*, C_3H_5, which has the same composition as the radical propenyl, the difference being represented by the formulæ:



$$\begin{array}{l} CH_2- \\ | \\ CH- \\ | \\ CH_2- \end{array}$$

Propenyl (triad).

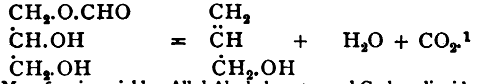


$$\begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2- \end{array}$$

Allyl (monad).

The allyl compounds in properties closely resemble the ethyl compounds. By the action of phosphorus iodide upon glycerol, the iodide C_3H_5I of a monovalent radical is obtained, from which a number of bodies have been derived, whilst the acrid substance *acroleïn*, formed in the destructive distillation of glycerol, is the aldehyde of this series.

Allyl Alcohol, $C_3H_5(OH)$, is formed in large quantity when glycerol is heated with oxalic acid to 190° ; *monoformin* is first produced, and this at a higher temperature yields allyl alcohol, water, and carbon dioxide :



$$\begin{array}{lcllll} \mathrm{CH_2.O.CHO} & & \mathrm{CH_2} & & & \\ \dot{\mathrm{C}}\mathrm{H.OH} & = & \ddot{\mathrm{C}}\mathrm{H} & + & \mathrm{H_2O} + \mathrm{CO_2}.\text{[1]} \\ \dot{\mathrm{C}}\mathrm{H_2.OH} & & \dot{\mathrm{C}}\mathrm{H_2.OH} & & & \end{array}$$

Monoformin yields Allyl Alcohol, water and Carbon dioxide.

It is a colourless liquid, boiling at 97^{c}, and possessing a pungent smell. It is oxidized in presence of air and platinum to acroleïn and acrylic acid, which stand to this alcohol in the same relation as aldehyde and acetic acid stand to ethyl alcohol : thus *acroleïn* is $CH_2 : CH.CHO$, and *acrylic acid* $CH_2 : CH.CO_2H$. Sodium dissolves in allyl alcohol, forming sodium allylate, the one atom of typical hydrogen in the alcohol being replaced by sodium. When this substance acts upon allyl iodide, an exchange of allyl and sodium takes place, *di-allyl ether*, $(C_3H_5)_2O$, being formed. *Allyl sulphide*, $(C_3H_5)_2S$, boils at 140°, and is remarkable as occurring in nature as the essential oil of garlic ; and the sulphide artificially prepared by acting on allyl iodide with an alcoholic solution of potassium sulphide, is identical in properties with the natural essence. In like manner *allyl thiocarbimide*, $CS.NC_3H_5$, isomeric with *allyl thiocyanate*, C_3H_5SCN, is found as the essential oil of black-mustard seed ; it can also be artificially prepared by treating allyl iodide with silver thiocyanate. It boils at 148°.

Acroleïn, C_3H_4O, is the aldehyde of allyl alcohol, and is formed when the alcohol is oxidized, two atoms of hydrogen being removed. Acroleïn is also produced by the abstraction of two molecules of water from glycerol :

$$C_3H_8O_3 - 2H_2O = C_3H_4O$$

hence its production when glycerol or a fat is heated.

---

[1] A single dot or short line between two atoms or groups of atoms signifies that the adjoining atoms are connected by single linkage. Where two dots or two short lines occur a double linkage of the atoms is denoted.

Acroleïn is a colourless liquid, boiling at 52°·4, and possessing a most pungent odour, which attacks the mucous membrane of the nose and eyes. It rapidly oxidizes to acrylic acid, $C_2H_3.CO_2H$, a substance possessing a close analogy with acetic acid, and which combines with hydrogen to form propionic acid.

Acrylic acid is the first term of a series of monobasic acids, the corresponding alcohols being for the most part unknown. They differ from the series of fatty acids in containing two atoms of hydrogen less.

Acrylic acid . . .	$C_3H_4O_2$.	Cimicic acid . . .	$C_{14}H_{26}O_2$.
Crotonic acid . . .	$C_4H_6O_2$.	Hypogæic acid . .	$C_{16}H_{30}O_2$.
Angelic acid . . .	$C_5H_8O_2$.	Oleic acid	$C_{18}H_{34}O_2$.
Pyroterebic acid . .	$C_6H_{10}O_2$.	Erucic acid . . .	$C_{22}H_{42}O_2$.

Crotonic acid occurs in croton oil, and angelic acid in the archangel-root, whilst angelic aldehyde, C_5H_8O, is contained in the essential oil of chamomile. Oleic acid exists, as has been said, in many oils, especially in almond oil, olive oil, and lard : this acid when acted upon by nitrous acid forms a new solid acid isomeric with oleic acid, and called *elaïdic acid.* Erucic acid is contained in rape-seed oil. The series receives the name of the *acrylic* or the *oleic acids.* The acids oxidize, in contact with the air, being converted into resinous bodies, and to this is due the property which these oils have of drying on exposure to the air.

Hydrocarbons of the Acetylene Series, C_nH_{2n-2}.

A series of non-saturated hydrocarbons homologous with acetylene (p. 89) exists ; they combine directly with two and four atoms of chlorine or bromine, and in the latter case form saturated compounds. These hydrocarbons are closely related to those of the ethylene series (p. 353). Thus, by acting upon the iodides or bromides of the ethylene series with alcoholic potash, we get the hydrocarbon of the acetylene series :

$$\underset{\text{Ethylene dibromide.}}{CH_2Br.CH_2Br} + 2KOH = \underset{\text{Acetylene.}}{CH\vdots CH} + 2KBr + 2H_2O.$$

The following is a list of the acetylene hydrocarbons :

		B.P.
Acetylene	C_2H_2	—
Allylene	C_3H_4	—
Crotonylene	C_4H_6	18°
Valerylene	C_5H_8	45°
Hexoylene	C_6H_{10}	80°
Œnanthylidene	C_7H_{12}	107°
Caprylidene	C_8H_{14}	133°
Decenylene	$C_{10}H_{18}$	165°
Benylene	$C_{15}H_{28}$	225°
Cetenylene	$C_{16}H_{30}$	280°

Acetylene, or *Ethine*, C_2H_2, is produced by the direct union of carbon and hydrogen, when the electric arc is made between two carbon poles placed in a vessel filled with pure hydrogen. It is also formed whenever a substance containing carbon and hydrogen undergoes incomplete combustion. The compounds of acetylene with certain metals are very remarkable; if this gas be passed into an ammoniacal solution of cuprous chloride, a red precipitate of *cuprous acetylide*, $C_2H_2Cu_2O$, is formed; whilst if an ammoniacal solution of a silver salt be used, a similar compound ($C_2H_2Ag_2O$), is precipitated as a white powder. Both these substances explode when heated or struck with a hammer; and both when heated with hydrochloric acid evolve acetylene gas:

$$C_2H_2Cu_2O + 2HCl = C_2H_2 + Cu_2Cl_2 + H_2O.$$

Allylene, C_3H_4, or *Propine*, is formed by the action of potash upon propylene dichloride. The other members of this series are powerfully smelling liquids which combine with two and four atoms of bromine.

Other hydrocarbons are known containing less hydrogen than those of the acetylene series. The most interesting of these is *dipropinyl*, $CH\equiv C—CH_2.CH_2.C\equiv CH$, which is isomeric with benzene, but has completely different properties, *e.g.* it combines readily with eight atoms of bromine.

TETRAD ALCOHOLS AND THEIR DERIVATIVES.

The most important tetrad alcohol is *erythrite* or *erythrol*, $C_4H_6(OH)_4$, a solid white substance found in certain lichens and fungi. When dissolved in cold concentrated nitric acid, erythrol forms the nitrate of this alcohol, $C_4H_6(NO_3)_4$, a body crystallizing in large white prisms, and decomposing with explosion on percussion. Treated with hydriodic acid, erythrol forms *secondary butyl iodide;*

$C_4H_6(OH)_4 + 7HI = C_4H_9I + 4H_2O + 3I_2$.
$CH_2(OH).CH(OH).CH(OH).CH_2(OH)$, Erythrol.
$CH_3.CH_2.CHI.CH_3$, Secondary butyl iodide.

HEXAD ALCOHOLS AND THEIR DERIVATIVES.

The derivatives of the hexad alcohols are of great importance as they include the group of the sugars, which stand in close relation to starch, cellulose, &c.

The best defined member of the series is *mannitol* or *mannite*, $C_6H_8(OH)_6$. This is a sugar-like substance contained in manna, the exudation of several species of ash. It is a white crystalline compound and has a pleasant sweet taste. That it is really a hexad alcohol is shown by the fact that it yields a hexanitrate, $C_6H_8(NO_3)_6$, and a hexacetate, $C_6H_8(OC_2H_3O)_6$. When it is treated with hydriodic acid it yields secondary hexyl iodide, which contains a normal chain of carbon atoms. Its constitution is therefore represented by the formula:

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH_2(OH).$$

Mannitol is also obtained by the reduction of the sugars mannose and fructose (or levulose), which are the corresponding aldehyde and ketone.

An examination of the above formula for mannitol shows that it contains 4 asymmetric carbon atoms, therefore the existence of isomerides similar to those of tartaric acid would be expected. A number of these have in fact been obtained. The more important are:

Dulcitol or *Dulcite*, $C_6H_8(OH)_6$. This is found in Madagascar manna, and is also a white crystalline substance, but has a less sweet taste than mannitol. It is also formed by the reduction of the sugar galactose, which is the corresponding aldehyde.

Sorbitol or *Sorbite* $C_6H_8(OH)_6$ is obtained from mountain-ash berries and also by the reduction of glucose (dextrose), which is the corresponding aldehyde.

LESSON XXXVIII

CARBOHYDRATES

UNDER this name a number of compounds have been classed, which all contain six atoms of carbon or a multiple of that number, together with hydrogen and oxygen in the proportion necessary to form water. They form a very important class of substances, occurring in the bodies of plants and serving as food for men and animals.

They are divided into three chief classes: (1) the glucoses or hexoses; (2) the saccharoses; (3) the amyloses. Each of these classes contains many distinct substances:

1. Glucoses or hexoses.	2. Saccharoses.	Amyloses. $(C_6H_{10}O_5)_n$.
Glucose or dextrose +	Cane-sugar +	Starch +
Fructose or levulose —	Lactose +	Glycogen +
Galactose +	Melezitose +	Dextrin +
Sorbose or sorbinose —	Maltose +	Inulin —
		Gums
		Cellulose
		Tunicin

One of the most important distinguishing physical properties of these bodies is their action on polarized light. Like tartaric acid, and many other substances, these compounds possess the power of rotating the plane of polarization, some to the right hand and some to the left: thus glucose, or grape-sugar, turns to the right; fructose, or levulose, to the left. The right-handed substances are marked in the preceding list with a +, the left-handed with a —.

The chemical constitution of the glucoses has now been for the most part determined, and some of them have been artificially prepared; new members of the series have also been synthetically obtained which have not as yet been found in nature. They are all aldehydes or ketones derived from the hexad alcohol:

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CH_2(OH)$$

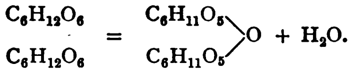
and have one of the two following structural formulæ:

(*a*) $CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).CHO.$
(*b*) $CH_2(OH).CH(OH).CH(OH).CH(OH).CO.CH_2.OH.$

The first formula contains four asymmetric carbon atoms, and the second three, so that we have a large number of different isomerides possible having the same structural formula. A discussion of the relations of all these isomerides, and of the numerous compounds derived from them is impossible in a work of this size, and only those compounds will be described here which have a practical or especial theoretical interest.

Substances are also known which are very similar in constitution and properties to the glucoses, but which only contain 5 atoms of carbon; these are known as *pentoses*. Similar compounds containing 7, 8, and 9 carbon atoms have been synthetically prepared.

The constitution of the saccharoses is closely connected with that of the glucoses, as they are derived by the union of two molecules of glucoses, with elimination of water:



$$\begin{matrix} C_6H_{12}O_6 \\ C_6H_{12}O_6 \end{matrix} = \left.\begin{matrix} C_6H_{11}O_5 \\ C_6H_{11}O_5 \end{matrix}\right> O + H_2O.$$

They therefore stand to the glucoses in the same relation as alcohol to ether.

The constitution of the amyloses is at present unascertained, and very few facts have been observed which give any indication of their structure.

THE HEXOSES, OR GLUCOSES

Glucose, *Dextrose*, *Grape-sugar* or *Starch-sugar*, $C_6H_{12}O_6$, is found in many kinds of fruit, in manna and honey mixed with fructose (levulose). It forms a normal constituent of blood, and white of egg, and exists in small quantity in healthy urine, whilst it is excreted in large quantities in that liquid in the disease termed diabetes.

Glucose is formed in many ways:

(1) By boiling starch or dextrin with dilute acids.

(2) By the action of malt upon starch (see Dextrin, p. 391).

(3) By the action of dilute acids upon cane-sugar (when it is formed together with fructose).

(4) By the action of acids upon many glucosides (*v. infra*).

Glucose is prepared by boiling starch with dilute sulphuric acid, adding chalk to neutralize the acid, and evaporating the liquid to a syrup when the sugar crystallizes. It may also be easily prepared by washing honey with ordinary alcohol: the fructose being more soluble is thus removed. It is soluble in its own weight of water, dissolves easily in dilute alcohol, and is not nearly so sweet as cane-sugar; the crystals contain one molecule of water, which they lose at 60°. Glucose immediately precipitates red cuprous oxide from alkaline cupric solutions (Fehling's solution); and the quantity of glucose present in a solution can be ascertained by employing a standard solution of alkaline copper salt. From silver salts the metal is deposited by glucose in the form of a mirror. Glucose, as already mentioned, rotates the plane of polarized light to the right.

Glucose is an aldehyde having the formula given on p. 384 under (*a*), the corresponding alcohol being sorbitol. It has been artificially prepared by means of a series of most interesting but complicated reactions. A substance has also been obtained synthetically which only differs from glucose inasmuch as it rotates the plane of polarization to the left as much as the latter does to the right. The name dextrose was given to glucose because of its dextro-rotatory action, but in view of the existence of the above lævo-isomeride it is inadvisable to retain that name, and a similar objection applies to the term levulose.

Fructose, Levulose, or *Fruit-sugar*, $C_6H_{12}O_6$ was for a long time only known as a syrup, but may be obtained crystalline by treatment with absolute alcohol; it is more soluble in water and alcohol than glucose, and is also sweeter. Its action on polarized light changes remarkably with the temperature. Fructose reduces cupric salts like glucose; it is obtained by neutralizing with lime the mixture of hexoses obtained by the action of sulphuric acid on cane-sugar. The fructose forms a compound with the lime, viz. $C_6H_{12}O_6.CaO+2H_2O$, which is a solid, whilst glucose forms a liquid compound. By decomposing this lime-compound with oxalic acid pure fructose is obtained. It is also obtained by the action of acids on inulin (p. 392).

Fructose has the structural formula given above on p. 384 under (*b*), and is a ketone derived from mannitol. It has also been obtained synthetically as well as the derivative of the same formula but with the opposite rotatory power.

Galactose is an aldehyde sugar of which dulcitol is the corresponding alcohol, and is obtained together with glucose by the action of acids on lactose or milk-sugar. It forms large sweet-tasting rhombic prisms.

Sorbose, or *Sorbinose* is a ketone-sugar and has not been so closely investigated as the others.

Mannose is the aldehyde sugar corresponding to mannitol, and was first prepared by oxidizing that substance; it has since been found in different plants, and is best obtained from ivory nut shavings by the action of acids.

Acrose, or *Inactive Fructose* is a combination of the two optically isomeric fructoses, and has been prepared synthetically in several ways; of these the most interesting is its formation, mixed with other products, by the polymerization of formaldehyde:

$$6CH_2O = C_6H_{12}O_6.$$

This result is especially valuable as being in confirmation of the theory that in the formation of sugars in plants from the carbon dioxide of the air, the latter is first reduced to formaldehyde, which then undergoes polymerization with formation of sugars.

THE SACCHAROSES

Cane-sugar, or *Saccharose*, $C_{12}H_{22}O_{11}$.—This important substance occurs in the juice of certain plants, especially the sugar-cane, beetroot, mallow, and sugar-maple; also, in smaller quantity, in honey and various kinds of fruit, together with a mixture of glucose and fructose. Sugar is prepared from the sugar-cane, which contains about 18 per cent. of sugar, by crushing out the juice by passing the cane between rollers; the juice is at once heated to about 60°, and a small quantity of milk of lime added for the purpose of precipitating the albuminous matter derived from the cane, the presence of which renders the juice liable to quick fermentation. The juice is then raised to the boiling-point, the scum which rises to the surface removed, and the clear liquid remaining boiled down in copper pans until it attains a certain consistency, when it is filtered through linen bags, and again evaporated to a syrup, which, on cooling, deposits crystals of moist or brown sugar. The mother-liquor is again evaporated, and again allowed to cool and deposit another crop of crystals; the dark-coloured uncrystallizable sugar is termed molasses, or treacle. The *refining* of sugar is a process conducted chiefly in England. The raw sugar is dissolved, and again boiled with lime and filtered. The filtered liquor is then decolorized by flowing through a thick bed of animal charcoal, and the colourless filtrate evaporated down to the point of crystallization, under diminished pressure, in vacuum pans. The object of this is to enable the syrup to boil at a lower temperature than it would do under the ordinary pressure, and thus to prevent formation of uncrystallizable sugar, and to avoid the charring and colouring of the syrup which otherwise takes place. The concentrated syrup is either allowed to crystallize in moulds, giving loaf sugar, or the small crystals are freed from adhering mother-liquor by quick drying in a hydro-extractor, or rapidly-revolving sieve. Much saving is attained by the use of the vacuum pan; and if its employment were universal in the colonies, where the sugar is first prepared, the formation of much treacle, or uncrystallizable sugar, would be avoided, and the profit to the planter proportionately increased. A method of treating the cane-juice has lately been proposed which bids fair to revolutionize the manufacture of raw sugar. It depends upon the fact, that by a peculiar plan of rapid evaporation the whole of the water can be got rid of, without charring the sugar, which is thus obtained as a solid mass, and all formation of treacle avoided.

A very large proportion of cane sugar is now manufactured from the beetroot, the process being carried out chiefly in France and Germany.

Sugar crystallizes in monosymmetric prisms, which phosphoresce when broken, and have a specific gravity of 1·606. It is soluble in one-third of its weight in cold, and in all proportions in hot water, and is nearly insoluble in alcohol and ether. Sugar melts at 160° to a colourless liquid, which solidifies on cooling to a colourless transparent mass (barley-sugar), and on standing becomes crystalline and opaque. When more strongly heated water is given off, and a dark-coloured mass called caramel is left behind. When acted on by nitric acid, either saccharic or oxalic acid is formed, according to the strength of the acid and the heat employed. Strong sulphuric acid converts sugar into a black mass, with evolution of sulphur dioxide. A mixture of these two acids in the cold acts on sugar to form a nitro-compound, $C_{12}H_{18}(NO_2)_4O_{11}$, an amorphous mass liable to explode on percussion.

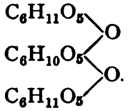
Cane-sugar does not reduce Fehling's solution in the cold, but does so on warming owing to the fact that it is then converted by the action of the alkali present into a mixture of glucose and fructose. The same reaction is brought about by heating it with dilute acids, showing that cane-sugar is derived from a molecule of glucose and a molecule of fructose by the elimination of a molecule of water. The exact manner in which the water is split off is unknown, but it has been shown that both the aldehyde group of glucose and the ketone group of fructose are altered in the process.

The mixture of glucose and fructose thus formed is called *invert-sugar*, as it has a lævo-rotatory action, in place of the dextro-rotatory action of the original cane sugar. The latter does not itself undergo fermentation, but must first be converted by the action of the ferment into invert-sugar, both the constituents of which can be readily fermented. Cane-sugar also combines with certain metallic oxides to form definite compounds termed *saccharosates*.

Lactose, or *Milk-sugar*, occurs only in the milk of mammalia, from which it is obtained in the crystalline state by evaporation. The crystals, which are rhombic, contain a molecule of water of crystallization, given off at 140°. Lactose dissolves in 6 parts of cold and 2·5 parts of boiling water; it does not possess nearly so sweet a taste as saccharose, feels gritty in the mouth, and is dextrorotary. Lactose does not ferment itself; but when much yeast is added, fermentation occurs after some time, mannitol being formed. In presence of cheese, &c. the lactic fermentation sets in. Dilute acids convert lactose into glucose and galactose, of which compounds it is therefore the anhydride. Lactose reduces an alkaline copper solution in the cold, precipitating cuprous oxide, but the quantity of this substance formed is not so great as when the same weight of glucose is employed. Lactose, when oxidized, yields mucic, saccharic, tartaric, and oxalic acids.

Maltose, $C_{12}H_{22}O_{11}+H_2O$, is obtained from starch by the action of malt diastase ; it is a white crystalline substance, which is converted by the action of dilute acids into glucose, and easily reduces alkaline solutions of cupric oxide.

Melitose, or *Raffinose*, $C_{18}H_{32}O_{16}+5H_2O$, is obtained from beet-root molasses, and crystallizes in thin needles or prisms. It is converted by dilute acids into glucose, fructose, and galactose, and must therefore be regarded as a double anhydride of these compounds,



All the sugars which contain the aldehyde group are converted by moderate oxidation into monobasic acids. Those obtained from the hexoses have all the structural formula :

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CH(OH).COOH.$$

Further oxidation converts them into dibasic acids of the structural formula :

$$COOH.(CH.OH)_4.COOH.$$

Of the latter the most important are *saccharic acid* and *mucic acid*. The first is formed by the oxidation of glucose and all substances which yield glucose on treatment with acids, and the latter by the oxidation of galactose and all galactose-forming substances.

FERMENTATION

This name has been given to a peculiar and interesting class of decompositions, which have long been known, but differ altogether from the ordinary chemical actions. Many organic bodies are capable of undergoing fermentation in presence of certain complicated substances termed *ferments*, giving rise to several products differing according to the nature of the fermented body and the ferment. Careful investigation has shown that two distinct kinds of ferments exist; one of these consists of *living organisms*, in the form of microscopic fungi, and hence termed *organized* ferments; the other being *non-organized*, and termed *soluble ferments*, or *enzymes*. Different kinds of ferments give rise to different products. Thus we have one organized ferment (yeast) which effects the alcoholic fermentation, another which sets up the lactic fermentation, a third producing the acetous fermentation, &c. In order that the organism of the ferment should grow, it must be supplied with proper food, especially with ammoniacal salts and alkaline phosphates: these are contained in the albuminous matter generally present in the liquid about to be fermented. In order that the fermentation should go on well, the temperature should be from 20° to 40°; at much higher, as at much lower temperatures, the vitality of the ferment is destroyed.

In many cases spontaneous fermentation sets in without the apparent addition of any ferment: thus wine, beer, milk, urine, &c., when allowed simply to stand exposed to the air, become sour or otherwise decompose. These changes are, however, not effected without the presence of vegetable or animal life, and are true fermentations: the *sporules*, or seeds of these living bodies, always float about in the air, and on dropping into the liquid begin to propagate themselves, and in the act of growing effect the changes known as fermentation. If the above liquids be left only in contact with air which has been passed through a red-hot platinum tube, thus destroying the living sporules; or if the air be simply filtered by passing through cotton-wool and the sporules prevented from coming into the liquid, it is found that these fermentable liquids may be preserved for any length of time without undergoing the slightest change.

The following are the five principal forms of fermentation:—

1. The alcoholic fermentation, producing chiefly alcohol and carbonic acid, effected by yeast.

2. The acetous fermentation, producing acetic acid, effected by a peculiar organism termed *mycoderma aceti.*

3. The lactic fermentation, yielding chiefly lactic acid, produced by the action of certain *bacteria* or rod-like organisms.

4. The butyric fermentation, yielding chiefly butyric acid, brought about by another species of *bacterium.*

5. The mucous fermentation, giving rise to gum and mannitol, and caused by a distinct vegetable growth.

Alcoholic Fermentation.—Most of the hexoses are able, when dissolved in presence of the yeast-plant (*Saccharomyces cerevisiæ*), to undergo fermentation, evolving mainly alcohol and carbonic acid :

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

About six per cent. of the glucose undergoes a different change, part being used as nourishment for the yeast, and another part forming glycerol and succinic acid. From 100 parts of glucose about 2·5 parts of glycerol are produced, and 0·6 to 0·7 of succinic acid, whilst 1·2 to 1·5 parts of cellulose and fatty matter are formed by the growth of the yeast. The alcoholic fermentation occurs best at a temperature of between 25° and 30°.

Non-organized ferments or *enzymes* are contained in many plants (see Glucosides) as well as in animal fluids, such as saliva, gastric juice. These ferments act like diastase, converting cane-sugar into glucose and fructose, and starch into glucose and dextrin, &c.

AMYLOSES BODIES AND GUMS, $(C_6H_{10}O_5)_n$.

Dextrin, $(C_6H_{10}O_5)_n$.—This substance, also called British Gum, is prepared by heating starch to about 150° : if a small quantity of nitric or hydrochloric acid is added to the starch, the transformation takes place much more rapidly. Dextrin and maltose are the first products of the action of malt extract upon starch. It rotates the plane of polarization strongly to the right. Dextrin is very soluble in water and insoluble in alcohol ; on boiling with dilute acids it is converted into glucose.

Gum Arabic.—The natural exudation from several species of acacias; it consists chiefly of the potassium and calcium salts of arabic acid, $C_{12}H_{20}O_{10}$.

Inulin.—A substance contained in the roots of various plants; it is intermediate between gums and starch, and yields fructose when boiled with dilute acids.

Glycogen, or *Animal Starch*, is an insoluble powder formed in the liver and placenta; it is easily converted into glucose.

Starch, $C_6H_{10}O_5$ (or some multiple of these numbers).—This important substance exists most widely diffused throughout the vegetable world. In its natural state it consists of a white powder composed of *granules;* whose appearance under the microscope is seen in Fig. 78, representing potato starch, Fig. 79 showing the granules of wheaten starch. These granules have a distinctly *organized* structure, and are of various sizes. The following are the diameters of the granules of some of the most important varieties of starch:

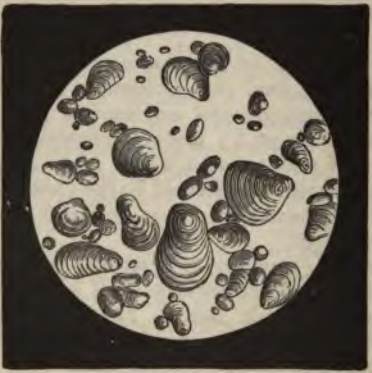


FIG. 78.

Potato .	0·185 mm.	Wheat	0·050 mm.	Millet . . .	0·010 mm.
Sago . .	0·070 ,,	Indian Corn .	0·030 ,,	Beetroot . .	0·004 ,,

Starch granules are insoluble in cold water, alcohol, and ether; but when they are heated with water above 60° they swell up and split open, forming a thick mass called starch paste. If this paste be boiled with a larger quantity of water, the particles of starch become so finely divided that they pass through a filter: and if boiled for a length of time, the solution becomes clear, and the starch is rendered soluble; and from this solution alcohol precipitates a white amorphous powder of soluble starch. When heated above 150° starch is converted into dextrin. Starch, in its insoluble and soluble modifications, forms with free iodine a deep blue compound, the colour of which is destroyed a little below 100°, but appears again on cooling. The production of this colour is characteristic of starch, and is not produced with dextrin or the other isomers of starch. When the soluble nitrogenous matter contained in malt, called *diastase*, acts upon starch, it forms maltose and dextrin; and by a longer action the dextrin is converted into glucose:

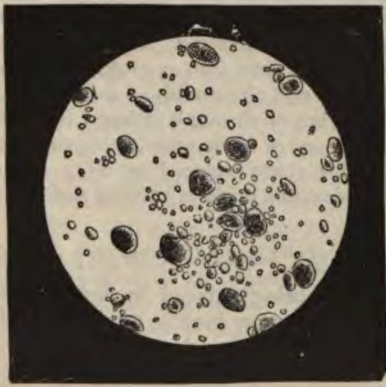


FIG. 79.

$$\overset{\text{Starch.}}{3C_6H_{10}O_5} + H_2O = \overset{\text{Maltose.}}{C_{12}H_{22}O_{11}} + \overset{\text{Dextrin.}}{C_6H_{10}O_5}.$$

The action of dilute sulphuric acid upon starch is similar to that of diastase. Strong sulphuric acid in the cold dissolves starch, forming a sulphuric ether. Nitric acid also dissolves it, and on adding water to the solution a white substance called *xyloidin* is precipitated: this is a nitrate, having the formula $C_6H_9O_4(NO_3)$.

Cellulose, $(C_6H_{10}O_5)_n$.—This is the colourless material of the woody fibre of young plants ; it may be obtained in the pure state from cotton or linen fibre by boiling out the impurities with alkali, alcohol, ether, &c. Cellulose is a white substance insoluble in water, alcohol, or ether, but soluble in an ammoniacal solution of cupric oxide. By the action of strong sulphuric acid, cellulose is converted either into an insoluble substance which is coloured blue by iodine, or into a soluble body like dextrin : if this acid solution be diluted with water and boiled, glucose is formed by fixation of one molecule of water. A useful substance is prepared under the name of *parchment paper*, by dipping sheets of unglazed paper into strong sulphuric acid.

Gun-cotton, $C_{12}H_{14}O_4(NO_3)_6$.—The action of strong nitric acid upon cellulose is interesting. If cotton wool be thrown in small portions at a time into a mixture of equal volumes of strong sulphuric and nitric acids, it does not undergo any apparent change, but on drying it is found to be very inflammable. It is a nitrate or nitric ether, being cellulose in which six atoms of hydroxyl are replaced by NO_3. By the action of ferrous chloride nitric oxide is evolved and cellulose again formed :

$$C_{12}H_{14}(NO_3)_6O_4 + 6H_2O = C_{12}H_{20}O_{10} + 6HNO_3,$$

the free nitric acid being reduced by ferrous salt to nitric oxide. Gun-cotton is now largely used as a substitute for gunpowder, as it offers many advantages :—

(1) The explosive force of gun-cotton is, weight for weight, greater than that of gunpowder. (2) The products of combustion of gun-cotton, being chiefly carbon dioxide and nitrogen, are not so apt to foul the gun. (3) When moistened it becomes incombustible, and only requires drying to render it again combustible.

Besides the hexanitrate the tri-and tetranitrate are known ; they dissolve readily in a mixture of alcohol and ether, yielding a solution which is termed *Collodion*, and is largely used for the purpose of forming a thin coating on glass to receive silver salts, upon which the photographic image is formed.

LESSON XXXIX

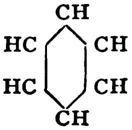
THE GROUP OF AROMATIC COMPOUNDS

UNDER this heading are classed a number of organic compounds differing from those already considered, inasmuch as they contain at least six atoms of carbon in the molecule and are relatively much richer in carbon than the compounds belonging to the fatty group. The term "aromatic" was applied to these substances because their first known repretatives all had an aromatic taste and smell.

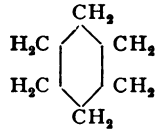
The simplest compound of this group is *Benzene* C_6H_6. A hydrocarbon of the same composition has already been described among the fatty compounds, viz., dipropinyl, which has the constitution $CH \vdots C \cdot CH_2 \cdot CH_2 \cdot C \vdots CH$ and readily combines with bromine to form the saturated additive compound $C_6H_6Br_8$. Benzene differs from dipropinyl inasmuch as it only forms additive products with bromine with difficulty, and under no circumstances does it take up more than 6 atoms of bromine, forming the compound $C_6H_6Br_6$, which behaves in all respects as a saturated compound. Under ordinary conditions moreover bromine acts on benzene with formation of substituted compounds such as C_6H_5Br, $C_6H_4Br_2$.

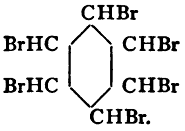
By the action of hydriodic acid benzene takes up 6 atoms of hydrogen forming a hydrocarbon C_6H_{12}, which is isomeric with the unsaturated hexylenes (p. 354) but behaves towards all reagents as a saturated compound.

To explain this behaviour Kekulé in 1865 suggested that in benzene the six carbon atoms are united together in the form of a closed chain instead of in an open one as with the fatty compounds, and that each carbon atom is in addition combined with an atom of hydrogen as shown in the following formula:



The formulæ of the hexahydride and hexabromide would then be as follows :





If the above formula for benzene is correct, then all the hydrogen atoms in benzene must be of equal value, and this has been experimentally proved. (See Roscoe and Schorlemmer, *Treatise on Chemistry*, Vol. III., Part III., p. 55.)

In the above formula of benzene each carbon atom appears to be a triad, instead of a tetrad as usual, or in other words, one of the valencies of each carbon atom is not accounted for. From the comparative stability of the compound towards bromine, these valencies cannot be free, but must neutralize one another in some way or another. The exact manner in which this takes place is not yet settled, although a number of theories have been proposed. It has, however, scarcely any bearing on the question of the constitution of the different isomerides, which may be deduced from the above simple formula without any reference to these combining units. Benzene must of course be regarded to some extent as an unsaturated compound, as it can under certain conditions take up other elements forming additive compounds, but in the vast majority of cases, both it and its numerous derivatives behave as saturated compounds, and they do not therefore belong to the same category as the unsaturated fatty compounds.

Compounds have also been obtained by synthesis which contain closed chains of three, four, and five carbon atoms ; these have chiefly a theoretical interest, and in their properties are intermediate between the fatty and aromatic groups, but are most nearly related to the former.

The members of the aromatic group are obtained from benzene by the partial or total replacement of the hydrogen by monad radicals, simple or compound. These compounds are far greater in number than those of the fatty group, and probably comprise more substances of technical importance, the great majority of which have been obtained during the last 25 years.

When one of the hydrogen atoms in benzene is replaced by chlorine we get chlorobenzene C_6H_5Cl, and as all the hydrogen atoms are equal in value, only one such compound can be obtained. In some respects this resembles the corresponding fatty chlorides such as C_2H_5Cl, but differs from them in containing the chlorine much more firmly combined, the chlorine not being readily displaced by other monad radicals. Again, if we replace a hydrogen atom in benzene by hydroxyl we get a *phenol*, $C_6H_5.OH$, which is distinguished from the fatty alcohols in the same way as chlorobenzene from the fatty chlorides; it does not form ketones or aldehydes on oxidation, and the hydrogen atom of the hydroxyl group is more readily replaced by metals, so that the phenols behave as quasi-acids, reacting with caustic alkalis to form a species of salt; thus phenol, C_6H_5OH, forms with caustic potash potassium phenate C_6H_5OK. An atom of hydrogen in benzene can also be replaced by NO_2, the radical of nitric acid, and the nitro-compound can be readily reduced to the amido-derivative containing the monovalent group NH_2. The most important mono-derivatives of benzene are the following:

Benzene	C_6H_6.
Monochloro-benzene	C_6H_5Cl.
Hydroxy-benzene or Phenol	C_6H_5OH.
Nitro-benzene	$C_6H_5NO_2$.
Amido-benzene, or Aniline	$C_6H_5NH_2$.

Several of these radicals may, however, replace several atoms of hydrogen in benzene, and hence the number of members of the aromatic series containing 6 atoms of carbon becomes very large.

In addition to these, a part of the hydrogen in benzene can be replaced by a carbon radical, and thus again a large number of compounds richer in carbon are added to the group. For example we are acquainted with a number of hydrocarbons forming an homologous series with benzene, each of which contains CH_2 more than the foregoing; these bodies are benzene in which 1, 2, or 3 atoms of hydrogen are replaced by methyl, CH_3.

Benzene	C_6H_6.
Methyl-benzene	$C_6H_5CH_3$.
Di-methyl-benzene	$C_6H_4(CH_3)_2$.
Tri-methyl-benzene	$C_6H_3(CH_3)_3$.
Tetra-methyl-benzene	$C_6H_2(CH_3)_4$.

In these compounds the hydrogen of the *benzene residue* can be replaced by radicals or elements just as in benzene itself, and the substitution products thus obtained possess properties strictly analogous to those obtained from benzene. But the hydrogen in the methyl can also be replaced, and it is important to notice that the compounds which are obtained in this way possess properties analogous to those of methyl itself and of the other alcohol radicals. The following isomeric series of compounds are thus obtained from methylbenzene or toluene:

Monochloro-toluene	$C_6H_4Cl.CH_3$.	Benzyl chloride	$C_6H_5.CH_2Cl$.
Cresol	$C_6H_4(OH).CH_3$.	Benzyl alcohol	$C_6H_5.CH_2(OH)$.
Nitro-toluene	$C_6H_4(NO_2).CH_3$.	Benzylamine	$C_6H_5.CH_2(NH_2)$.
Amido-toluene	$C_6H_4(NH_2).CH_3$.		

Those on the left behave as aromatic compounds, and those on the right chiefly as fatty compounds.

Benzyl alcohol yields on oxidation benzaldehyde, $C_6H_5.CHO$, and benzoic acid, $C_6H_5.CO_2H$. From di- and tri-methyl-benzene similar series are obtained, and as the other well-known alcohol radicals may be substituted for methyl, and as these again give rise to similar substitution products, it is clear that the possible number of the aromatic series is not only extremely large, but that a great variety of isomerides must occur in the group.

Thus, di-methyl-benzene, $C_6H_4(CH_3)_2$, is isomeric with ethyl-benzene, $C_6H_5(C_2H_5)$, whilst the four following hydrocarbons have the composition C_9H_{12}.

Tri-methyl-benzene	$C_6H_3(CH_3)_3$.
Propyl-benzene	$C_6H_5(C_3H_7)$.
Methyl-ethyl-benzene	$C_6H_4(CH_3)C_2H_5$
Iso-propyl-benzene	$C_6H_5.CH(CH_3)_2$.

As these hydrocarbons resemble each other very closely, it is of great importance to have a means of recognizing the number of hydrocarbon radicals they contain. This is easily effected by oxidizing them either by dilute nitric or chromic acid, when each of the alcohol radicals attached to the benzene residue is converted into carboxyl; thus toluene or methylbenzene, $C_6H_5.CH_3$, ethylbenzene, $C_6H_5.C_2H_5$, amylbenzene, $C_6H_5.C_5H_{11}$, all yield on oxidation one and the same acid, $C_6H_5.CO_2H$, viz. benzoic acid. Dimethylbenzene, isomeric with ethylbenzene, yields on oxidation at first a monobasic acid, viz. a toluic acid, $C_6H_4(CH_3).CO_2H$, and afterwards a dibasic acid, $C_6H_4(CO_2H)_2$.

Another characteristic of the benzene derivatives is the existence of three classes of bi-derivatives of the general formulæ $C_6H_4X_2$, C_6H_4XY. Thus three isomeric dibromobenzenes $C_6H_4Br_2$, are known, three isomeric dimethyl-benzenes, $C_6H_4(CH_3)_2$, and three toluic acids, $C_6H_4(CH_3)CO_2H$, and also three dicarboxylic acids, $C_6H_4(COOH)_2$, etc. Three isomeric tri-derivatives of the general formula, $C_6H_3X_3$, can also exist. This species of isomerism is characteristic of benzene and compounds constituted similarly to this hydrocarbon, the generally received explanation of which will be given later on (p. 409).

All monoderivates of benzene may be regarded as compounds of the radical C_6H_5 with monad groups just as with the corresponding mono-substituted fatty hydrocarbons. The radical C_6H_5 is termed *phenyl*.

BENZENE AND ITS MONOSUBSTITUTION PRODUCTS.

Benzene, or *Benzol*, C_6H_6.—This body has been prepared from its elements by synthesis, by heating acetylene, obtained by the direct union of carbon and hydrogen, nearly to a red-heat, benzene being formed:

$$3C_2H_2 = C_6H_6.$$

The ordinary source of benzene is, however, the light oil obtained by the destructive distillation of coal, of which it forms a considerable part. It is a colourless liquid, which refracts light powerfully, boils at 80·5°, and solidifies on cooling to crystals which melt at 4·5°. It is also obtained by distilling benzoic acid with slaked lime. Benzene is attacked by chlorine, with formation of several chloro-benzenes. These are substitution products, *i.e.* they are $C_6H_5Cl, C_6H_4Cl_2$, &c.,

but by acting on boiling benzene with chlorine, or on the cold liquid in presence of aqueous caustic soda, addition products are formed, the final one being $C_6H_6Cl_6$, *benzene hexachloride*, which corresponds to the hexabromide already mentioned.

Benzenesulphonic acid, $C_6H_5.SO_3H$. When benzene is dissolved in concentrated solution the following reaction takes place

$$C_6H_6 + OH.SO_2.OH = C_6H_5.SO_2.OH + H.OH.$$

The group $SO_2.OH$ or SO_3H is known as the sulphonic acid group, and the above compound is therefore benzenesulphonic acid. The formation of these sulphonic acids by the action of sulphuric acid is very characteristic of aromatic compounds. Similar derivatives are known in the fatty series but are only obtained indirectly.

Benzenesulphonic acid is a white crystalline compound, is a monobasic acid, and is very stable, resisting the action of water and solutions of caustic alkalis. When its potassium salt is fused with caustic potash it is decomposed, the group SO_3K is replaced by OH, and phenol formed, thus :

$$C_6H_5SO_3K + KHO = C_6H_5OH + K_2SO_3.$$

This is a method of wide applicability for the preparation of various phenols.

Phenol, or *Carbolic Acid*, $C_6H_5.OH$.—This is a white solid crystalline body, melting at 42°, and boiling at 182°, found in the heavy coal-tar oils. It dissolves in the alkalis, forming phenates, but does not possess an acid reaction; from the strong solution of sodium phenate the phenol may be isolated by addition of an acid, when it separates out as an oily liquid. In this way phenol is extracted from coal tar, and is finally purified by fractional distillation. The most important property of this body is its powerful antiseptic action, and it is much used as a disinfectant, both alone and combined with lime. Benzene is formed when phenol vapour is passed over heated zinc dust :

$$C_6H_5OH + Zn = C_6H_6 + ZnO.$$

Phenol is sometimes called phenyl alcohol, but it differs *from a true* alcohol in several respects ; thus, it is not readily oxidized, and yields neither an aldehyde, a ketone, nor an acid. Nearly all phenols give certain colour reactions with ferric chloride solution; ordinary phenol produces a violet coloration.

Trinitrophenol, or *Picric Acid*, $C_6H_2(NO_2)_3OH$.—When phenol is acted upon by nitric acid, 1, 2, or 3 atoms of hydrogen may be substituted by NO_2. Picric acid is a bright yellow crystalline body, very soluble in water; it is obtained by the action of nitric acid upon many other substances containing the aromatic nucleus besides carbolic acid and its derivatives. Phenol itself has only weak acid properties, but the entrance of three nitro-groups into the molecules increases the acid nature of the substance so much, that picric acid forms salts quite as stable as those of most acids containing the carboxyl group. Picric acid is employed in the arts as a yellow dye for silk and woollen goods, also in the manufacture of explosives.

Nitro-benzene, $C_6H_5(NO_2)$, is produced when benzene is treated with nitric acid; it is a substitution product in which one hydrogen atom of benzene is replaced by NO_2, and forms a light yellow liquid smelling like oil of bitter almonds, insoluble in water, and boiling at 205°. In contact with reducing agents, nitro-benzene undergoes the following reduction to *aniline*, in which the monad group (NO_2) is converted into the monad group (NH_2):

$$\underset{\text{Nitro-benzene.}}{C_6H_5(NO_2)} + 3H_2 = \underset{\text{Aniline.}}{C_6H_5(NH_2)} + 2H_2O.$$

Aniline, or *Amido-benzene*, $C_6H_5(NH_2)$.—This important body is benzene in which one atom of hydrogen is replaced by the monad group (NH_2); and it is therefore properly called amido-benzene. The mode of preparing aniline from benzene has just been mentioned, the reduction of nitrobenzene being generally effected by a mixture of iron-filings and hydrochloric acid, when the chlorides of iron and of aniline are formed; the aniline is liberated by addition of an alkali, and is separated by distillation. It is also formed by the action of potash on indigo (p. 422), and is found amongst the products of the destructive distillation of coal.

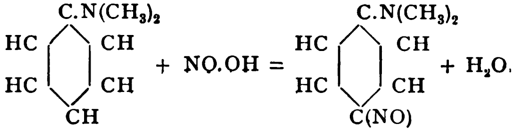
Aniline is a colourless liquid possessing a peculiar smell; its specific gravity at 0° is 1·036, and it boils at 183°. It is nearly insoluble in water, but dissolves in alcohol and ether : it unites with acids to form definite salts, but does not turn red litmus paper blue. Crude aniline is manufactured now on a very large scale for the preparation of the so-called *aniline colours*, so generally used in calico-printing and woollen- and silk-dyeing. The smallest trace of aniline may be easily detected by adding the substance to an aqueous solution of an alkaline hypochlorite, when a splendid violet coloration is produced.

The hydrogen atoms in the amido-group of aniline can be replaced by fatty alcohol radicals, and also by additional phenyl groups. Thus by heating aniline with methyl chloride we get a mixture of *methylaniline* $C_6H_5.NH.CH_3$ and *dimethylaniline* $C_6H_5.N(CH_3)_2$; both of these are liquids boiling at 191° and at 192° respectively, and are used in the colour industry.

These three compounds, aniline, $C_6H_5.NH_2$, methylaniline $C_6H_5.NH.CH_3$, and dimethylaniline $C_6H_5.N(CH_3)_2$ stand to one another in the same relation as the primary, secondary, and tertiary fatty amines. When primary aromatic amido-compounds are treated with nitrous acid, the group is converted into hydroxyl, as with the primary fatty compounds, but with the difference that an intermediate series of compounds, known as the *diazo-compounds* (see below), is formed. With the secondary amido-compounds the H of the NH group is replaced by the group NO : thus methylaniline yields *methyl phenylnitrosamine :*

$$C_6H_5.NH.CH_3 + NO.OH = C_6H_5N(NO)CH_3 + H_2O.$$

The tertiary fatty amines are unacted on by nitrous acid, but with the corresponding aromatic compounds, nitroso-derivatives are obtained, in which the nitroso-group replaces one of the hydrogen atoms of the benzene ring. Thus dimethylaniline behaves in the following manner yielding nitrosodimethylaniline :—



Dimethylaniline, like other tertiary amines, combines with methyl iodide forming the ammonium compound *trimethyl-phenyl ammonium iodide* $(CH_3)_3C_6H_5,N.I$ which yields the corresponding *hydroxide* $(CH_3)_3C_6H_5.N.OH$, on treatment with silver oxide.

Diphenylamine or *Phenylaniline*, $(C_6H_5)_2NH$, is prepared by heating aniline hydrochloride with aniline :

$$C_6H_5.NH_2 + C_6H_5.NH_3Cl = (C_6H_5)_2NH_2Cl + NH_3.$$

It crystallizes in monosymmetric plates, melts at 54°, and boils at 302°. It is also used in the colour industry.

The hydrogen atoms of the amido-group in aniline and similar compounds may be replaced by acid radicals, such as *acetyl*, giving rise to compounds termed *anilides*. Thus when aniline is boiled with acetic acid or anhydride, it yields *acetanilide*, $C_6H_5.NH.CO.CH_3$, which forms lustrous tablets melting at 112°.

Diazo- and Azo-compounds of Benzene.

It has already been mentioned (p. 402) that when a primary amine is acted upon by nitrous acid, the NH_2 group is replaced by hydroxyl and an alcohol formed. In the case of the aromatic amines the action of nitrous acid results in the formation of a series of intermediate compounds, known as *diazo-compounds*, which are of especial interest both theoretically and practically. When, for instance, nitrous acid is allowed to react upon aniline nitrate, *diazobenzene nitrate*, $C_6H_5.N_2.NO_3$, is formed, thus :

$$C_6H_5NH_2.NO_3H + NO.OH = C_6H_5.N_2.NO_3 + 2H_2O.$$

This compound is a colourless crystalline substance, which explodes when heated or on percussion. It may serve as an example of other similar compounds, which may be regarded as the salts of a base, $C_6H_5.N_2.OH$, the hypothetical diazobenzene, containing the monovalent group, $C_6H_5-N=N—$.

These salts when boiled with water are decomposed, nitrogen is set free, and the group (HO) replacing the N_2 in the benzene residue forms a phenol, thus :

$$C_6H_5.N_2.NO_3 + HOH = C_6H_5.OH + N_2 + HNO_3.$$

A diazobenzene salt undergoes a similar decomposition when boiled with hydriodic acid, iodobenzene being formed:

$$C_6H_5.N_2.NO_3 + HI = C_6H_5I + N_2 + HNO_3;$$

whilst, when boiled with absolute alcohol, the alcohol is reduced to aldehyde, nitrogen set free, and the N_2 of the diazo-compound replaced by hydrogen; thus diazobenzene sulphate can be converted into benzene:

$$C_6H_5.N_2.SO_4H + C_2H_6O = C_6H_5H + H_2SO_4 + N_2 + C_2H_4O.$$

If a diazo-salt be treated with cuprous chloride, bromide, or cyanide, the diazo-group is replaced by chlorine, bromine, or cyanogen. In this manner diazobenzene may be converted into C_6H_5Cl, C_6H_5Br, and $C_6H_5.CN$.

The diazo-compounds are therefore a most important class of substances, as from them we can so readily obtain such a large number of other benzene derivatives.

When a diazobenzene salt, for instance the chloride, is boiled with aniline, *diazo-amidobenzene*, $C_6H_5.N_2.NH.C_6H_5$ is formed:

$$C_6H_5.N_2.Cl + 2C_6H_5NH_2 = C_6H_5.N_2.NH(C_6H_5) + C_6H_5NH_2.HCl.$$

This compound is also produced by the action of nitrogen trioxide on an excess of aniline, and when heated in presence of a salt of aniline it undergoes an intermolecular change, whereby it is converted into an isomeride *amido-azobenzene*, $C_6H_5.N_2.C_6H_4(NH_2)$, which is non-explosive, dyes silk yellow, and is known as *Aniline yellow*.

Azobenzene, $C_6H_5.N_2.C_6H_5$, of which aniline yellow is a derivative, is a bright red crystalline body obtained by the reduction of nitro-benzene under certain conditions. The azo-compounds are distinguished from the diazo-compounds by their much greater stability, and by containing two benzene or similar groups attached to the nitrogen group, $-N=N-$; while the diazo-compounds contain only one such group, but in addition contain a negative element or radical.

The following are some of the more important *Azo-colours* which are nearly allied to amido-azobenzene.

Chrysoïdine, or *Diamido-azobenzene*, $C_6H_5N_2\ C_6H_3(NH_2)_2$. The hydrochloride of this base crystallizes in brown octahedra, and dyes wool and silk a bright orange.

Bismarck-brown, or *Manchester-brown*, is the hydrochloride of triamido-azobenzene, $H_2N.C_6H_4.N_2C_6H_3(NH_2)_2$, and is largely used as a brown dye.

The *Tropaeolins* are also azo-dyes, which contain the sulphonic acid group SO_3H, and are obtained from sulphanilic acid (anilinesulphonic acid) $C_6H_4(SO_3H)NH_2$.

For a description of the other azo-colours a larger work must be consulted.

Phenylhydrazine, $C_6H_5.NH.NH_2$. This compound, which stands in the same relation to hydrazine (p. 75) as aniline to ammonia, is prepared by the reduction of diazobenzene chloride. It is a colourless substance which quickly becomes yellow in the air, melts at 23°, and boils at 241-242°. It is one of the most important reagents in organic chemistry, as it combines with all aldehydes and ketones forming compounds termed *hydrazones*, which as a rule crystallize well, and are made use of to isolate aldehydes and ketones from a mixture of other compounds. Acetone and phenylhydrazine react as follows:

$$(CH_3)_2CO + H_2N.NH.C_6H_5 = (CH_3)_2C : N.NH.C_6H_5 + H_2O.$$

Phenylhydrazine is a monacid base; its *hydrochloride* $C_6H_5.NH.NH_3Cl$, crystallizes in slender lustrous plates.

Toluene and its Derivatives.

Toluene, or *Methylbenzene*, C_7H_8, or $C_6H_5(CH_3)$.—This hydrocarbon, which like benzene occurs in coal oils, boils at 111°, and does not solidify at $-20°$; it is also formed by the distillation of toluic acid, $C_6H_4(CH_3)COOH$, with excess of lime. By the action of oxidizing agents it is converted into benzoic acid:

$$C_6H_5.CH_3. + O_3 = C_6H_5COOH + H_2O.$$

BENZYL GROUP.

When chlorine acts on toluene in the cold chlorotoluene is formed, one atom of hydrogen in the benzene residue being replaced by chlorine. This and similar bodies will be found described under the head, "Di-substitution Products of Benzene." If chlorine be passed into boiling toluene, one of the hydrogen atoms of the methyl group is replaced, and *Benzyl Chloride*, $C_6H_5.CH_2Cl$, boiling at 176°, is formed. From this a number of benzyl compounds can be prepared. Of these the more important are:—

Benzylamine, $C_6H_5.CH_2NH_2$, a colourless liquid, isomeric with toluidine (p. 411) boiling at 185°, obtained by the action of ammonia upon benzyl chloride. It is a true amine, and gives rise to corresponding secondary and tertiary amines.

Benzyl Alcohol, $C_6H_5.CH_2(OH)$, obtained by the action of alcoholic potash[1] or nascent hydrogen, on oil of bitter almonds (which is the aldehyde of the series). It is an oily colourless liquid, boiling at 207°. Oxidizing agents convert it first into the aldehyde, C_7H_6O, and lastly into the acid of the series, $C_7H_6O_2$, benzoic acid.

Benzaldehyde, or *Oil of Bitter Almonds*, C_6H_5CHO.—This oil does not exist already formed in bitter almonds, but is the result of the decomposition of a glucoside termed amygdalin contained in the almond (p. 433).

It can likewise be obtained by distilling a benzoate and a formate, in this respect resembling the aldehydes of the fatty group; it also forms a crystalline compound with hydrogen sodium sulphite. It is also prepared by heating *benzylene dichloride*, $C_6H_5CHCl_2$, formed by the action of chlorine on boiling benzyl chloride, with mercuric or lead oxides. Bitter almond oil is a colourless strongly-smelling liquid, boiling at 180°; the commercial substance (used in cookery) is very poisonous, as it invariably contains an admixture of hydrocyanic acid. On exposure to air or oxygen, or when acted upon by oxidizing agents, it is converted into benzoic acid. Benzaldehyde may be regarded as toluene or methyl-benzene in which two atoms of hydrogen of the methyl are replaced by one atom of oxygen, $C_6H_5(CHO)$; whilst *benzoyl chloride*, C_6H_5COCl, is the last named substance in which the one remaining atom of hydrogen in the methyl is replaced by chlorine. The vapour of bitter almond oil decomposes into benzene and carbon monoxide when passed through a red-hot tube; and benzoyl chloride is

---

[1] By heating an aldehyde of the aromatic series with caustic alkali, simultaneous oxidation and reduction frequently take place, thus:

$$\underset{\text{Benzaldehyde.}}{2C_6H_5.COH} + KOH = \underset{\text{Benzoic Acid.}}{C_6H_5.CO_2K} + \underset{\text{Benzyl Alcohol.}}{C_6H_5.CH_2(OH)}.$$

formed by the direct action of carbonyl chloride on benzene, in presence of aluminium chloride, the monad group (COCl) changing places with one atom of hydrogen, thus :

$$\underset{\text{Carbonyl Chloride.}}{COCl_2} + \underset{\text{Benzene}}{C_6H_6} = \underset{\text{Benzoyl Chloride.}}{C_6H_5(COCl)} + HCl.$$

Benzoyl chloride can also be formed by the action of phosphorus pentachloride upon benzoic acid; it is a colourless liquid, which boils at 199°, and has a very penetrating smell, the vapour attacking the eyes violently. It is decomposed by water yielding benzoic acid.

Benzoic Acid, $C_6H_5.CO_2H.$, is found in many resins, especially in gum benzoin; it also occurs in the urine of cows, and in the putrefied urine of man and other animals; it can be obtained by the oxidation of benzyl alcohol and bitter almond oil; also synthetically, by acting upon monobromobenzene with sodium and carbon dioxide :

$$C_6H_5Br + Na_2 + CO_2 = C_6H_5.CO_2Na + NaBr.$$

Benzoic acid may be easily prepared by heating gum benzoin, when the acid sublimes in pearly white plates ; it melts at 120° and boils at 250°. Benzoic acid forms a series of salts, most of which are soluble : the ferric benzoate falls as an insoluble red precipitate when sodium benzoate is added to ferric chloride.

Benzoyl Oxide, or *Benzoic Anhydride*, $(C_7H_5O)_2O$, is obtained by acting upon potassium benzoate with benzoyl chloride, thus :

$$C_6H_5.CO(OK) + C_6H_5.COCl = (C_6H_5.CO)_2O + KCl.$$

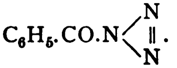
It is a solid substance, melting at 42°, and boiling at 360°; it is soluble in alcohol and ether. Several mixed anhydrides are also known : thus we have acetyl benzoate, $C_2H_3O.O.C_7H_5O$.

Benzoyl Peroxide, $(C_7H_5O)_2O_2$.—A well-crystallized substance, obtained by the action of barium peroxide on benzoyl chloride: it explodes when heated, and resembles acetyl peroxide (p. 340).

Benzoylhydrazine, $C_6H_5.CO.NH.NH_2$. When ethyl benzoyl glycollate, $C_6H_5.CO.O.CH_2.CO_2C_2H_5$, is treated with hydrazine hydrate, N_2H_4,H_2O (p. 75), the following reaction takes place :

$$C_6H_5.CO.O.CH_2.CO_2C_2H_5 + 2N_2H_4$$
$$= \underset{\text{Benzoylhydrazine.}}{C_6H_5.CO.NH.NH_2} + \underset{\text{Ethyl hydrazidoacetate.}}{NH_2.NH.CH_2.CO_2C_2H_5} + H_2O.$$

Benzoylhydrazine crystallizes in large plates melting at 112°, and on treatment with nitrous acid yields *benzoyl azoimide*



$C_6H_5.CO.N\left<\begin{matrix}N\\ \|\\ N\end{matrix}\right.$. The latter forms colourless prisms melting at 29-30°, and is converted by acids into azoimide, N_3H (p. 75).

Hippuric Acid, $C_9H_9NO_3$, is contained in the urine of horses and herbivorous animals. It can also be artificially prepared by the action of benzoyl chloride on glycocoll or amido-acetic acid, showing that hippuric acid is benzoyl amido-acetic acid, thus :

Glycocoll.

$$\begin{matrix}CH_2.NH_2\\ |\\ CO\ OH\end{matrix}$$

Hippuric Acid.

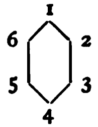
$$\begin{matrix}CH_2.NH.CO.C_6H_5\\ |\\ CO.OH.\end{matrix}$$

By passing through the animal body benzoic acid is converted into hippuric acid.

DI- AND TRI- SUBSTITUTION PRODUCTS OF BENZENE.

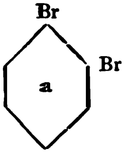
Hitherto only the monosubstitution products of benzene have been considered : of these only one modification exists, inasmuch as all the six hydrogen atoms in benzene are of equal value. In the case of the di- and tri- substitution products different isomerides occur ; it has been found in the case of those di-substitution products which have been thoroughly investigated that three and only three isomerides exist, and the same is true of the tri-substituted compounds so long as the three substituent groups are the same. Thus we are acquainted with three dibromo- and three tribromo-benzenes.

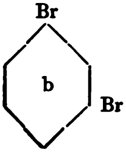
This experimental result is in full agreement with the theory of the constitution of benzene. If we represent benzene graphically as a hexagon at the angles of which carbon atoms are placed, and number these carbon atoms as shown in the formula given below, it is easy to see that three dibromobenzenes should exist in which the two bromine atoms occupy the positions 1.2, 1.3, 1.4, respectively:

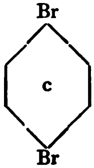


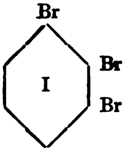
No other isomerides are possible, as the positions 1.5 and 1.6 are identical with 1.3 and 1.2.

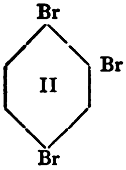
In the same way it will be seen that with the tribromobenzenes three and only three positions of the bromine atoms are possible, viz. 1.2.3, 1.3.4, and 1.3.5. We get therefore the following graphic formulæ for these compounds :—

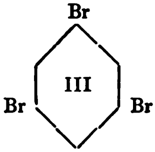












It is, however, not only possible to explain the existence of these three isomerides but also to ascertain which of the positions the groups in such a compound actually occupy. An examination of the above six formulæ shows that from the 1.2 dibromobenzene, we can obtain 1.2.3, and 1.2.4, tribromobenzene, by further displacement of a hydrogen atom by bromine; from 1.3 dibromobenzene we could get 1.2.3, 1.3.4, and 1.3.5 tribromobenzene, whilst 1.4 dibromobenzene would only yield 1.3.4 tribromobenzene. In other words, the 1.2 dibromobenzene can yield two tribromobenzenes on further bromination, the 1.3 compound three, and the 1.4 compound only one. This has been experimentally carried out with the three dibromobenzenes, and it is found that the one boiling at 224° is the 1.2 compound, that boiling at 219·4° the 1.3 compound, and that melting at 82·3° the 1.4 compound. This being once fixed, the constitution of other disubstitution products may be ascertained by synthesizing them from one of the dibromobenzenes.

In place of the numbers 1.2, 1.3, 1.4, the terms *ortho-*, *meta-*, and *para-*, are often employed as prefixes, and in the case of the trisubstitution compounds, the positions 1.2.3, 1.3.4, and 1.3.5 are frequently spoken of as *adjacent*, *asymmetric*, and *symmetric* respectively. Instead of writing these prefixes in full the following contractions are frequently employed :

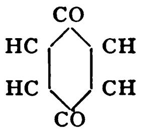
ortho = *o*
meta = *m*
para = *p*
adjacent = *v*
asymmetric = *as*
symmetric = *s*

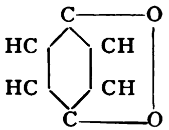
Among the more important disubstitution derivatives may be mentioned the dihydroxybenzenes.

Orthodihydroxybenzene or *Catechol* (*Pyrocatechin*), $C_6H_4(OH)_2$, stands in the same relation to phenol as glycol to alcohol. It is obtained by the action of potash on orthoiodophenol, or of hydriodic acid on *guiacol*, which is its methyl ether, and occurs in beechwood tar creosote. Catechol is also formed in the dry distillation of catechu, many resins, and wood.

Metadihydroxybenzene or *Resorcinol*, $C_6H_4(OH)_2$, is prepared by heating benzene with sulphuric acid, and fusing the *benzenemetadisulphonic acid*, $C_6H_4(SO_3H)_2$, thus formed with potash. It crystallizes in rhombic prisms and melts at 118°.

Paradihydroxybenzene, *Quinol*, or *Hydroquinone*, $C_6H_4(OH)_2$, is prepared by the dry distillation of quinic acid, and by the moderate oxidation of aniline. It is largely used in photography as a developer. On oxidation it readily loses two atoms of hydrogen forming *quinone*, $C_6H_4O_2$, which sublimes in beautiful yellow needles with a penetrating smell, and has a constitution represented by one of the following formulæ :—





Its *tetrachloro-derivative*, generally known as *chloranil*, $C_6Cl_4O_2$, is obtained in golden scales by the action of hydrochloric acid and potassium chlorate on quinone, phenol, and other aromatic compounds. It is a very stable body, and is not acted on by concentrated sulphuric or nitric acids, or by *aqua regia.*

Amidotoluene or Toluidine, $C_6H_4(CH_3)NH_2$, exists in three isomeric forms, one of which is solid, and always occurs in commercial aniline; it is indeed a necessary ingredient for the preparation of the rosaniline colours (p 417). It melts at 40° and boils at 202°. The toluidines are isomeric with benzylamine, $C_6H_4.CH_2.NH_2$ (p. 406).

Cresol, $C_6H_4(CH_3)OH$, is the next homologue of phenol, and exists in three modifications, all of which are contained in coal-tar.

SALICYLIC, OR HYDROXYBENZYL GROUP.

The members of this group are closely connected with the benzyl and the benzoyl series, differing from them by the substitution of an atom of hydrogen in the benzene residue by hydroxyl (OH).

Salicyl Aldehyde, $C_6H_4\left\{\begin{matrix}COH\\OH\end{matrix}\right.$.—The volatile essential oil of the flowers of the meadow-sweet (*Spiræa ulmaria*) consists mainly of this aldehyde. It is also formed by the oxidation of *Saligenin*, $C_7H_8O_2$, or orthohydroxybenzyl alcohol, a body derived from salicin, a bitter principle found in willow bark. The close relations of saligenin, orthocresol, and benzyl alcohol are shown in the following formulæ:

Saligenin.	Orthocresol.	Benzyl Alcohol.
$C_6H_4(OH)CH_2OH$;	$C_6H_4(OH)CH_3$;	$C_6H_5CH_2OH$.

Salicylic Acid, or *Orthohydroxybenzoic Acid* (1·2), C_6H_4OH CO_2H, is found together with the aldehyde in the oil of *Spiræa*, and is formed by the oxidation of salicyl aldehyde, &c. It is now obtained on the large scale by synthesis from phenol. Sodium phenate is first prepared by dissolving phenol in caustic soda, and then passing carbon dioxide into the dry salt, which is slowly heated up to 180°.

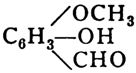
$$\underset{\text{Sodium Phenate.}}{2C_6H_5ONa} + CO_2 = \underset{\text{Sodium Salicylate}}{C_6H_4ONa.CO_2Na.} + C_6H_5OH.$$

On heating, salicylic acid sublimes, and at a higher temperature decomposes into phenol and carbon dioxide. It crystallizes in large four-sided prisms, which melt at 155°; its aqueous solution gives a characteristic violet colour with ferric salts, and it occurs in the oil of winter-green (*Gaultheria procumbens*) as the methyl ether $C_6H_4.(OH)CO_2.CH_3$. Salicylic acid possesses valuable disinfecting and medicinal properties.

Parahydroxybenzoic (1·4) and *Metahydroxybenzoic* (1:3), *Acid* are two isomerides of salicylic acid; the meaning of the numbers (1:2), (1:4), (1:3), placed after the names of these acids has already been explained.

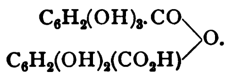
Protocatechuic Acid, or *Dihydroxybenzoic Acid*, $C_2H_3(OH)_2.CO_2H$, is formed when different resins and plant extracts, such as catechu, are fused with alkali, and crystallizes in lustrous needles, the aqueous solution of which is coloured green by ferric chloride. The corresponding *aldehyde*, $C_6H_3(OH)_2CHO$, is formed by the action of chloroform on an alkaline solution of catechol:

$$C_6H_4(OH)_2 + CHCl_3 + H_2O = C_6H_3(OH)_2CHO + 3HCl.$$

If in place of catechol we take catechol methyl ether (guiacol) the corresponding *methylprotocatechuic aldehyde* or *vanillin*,  $C_6H_3\begin{cases}OCH_3\\OH\\CHO\end{cases}$ is formed; it crystallizes in white needles and is contained in vanilla-root.

Gallic Acid, or *Trihydroxybenzoic Acid*, $C_6H_2(OH)_3CO_2H$, is contained in gall-nuts, and is also formed by heating di-iodosalicylic acid or bromoprotocatechuic acid with potash. It forms white needles, and gives a bluish-black precipitate with ferric chloride. On heating it decomposes into *pyrogallol* or *trihydroxybenzene*, $C_6H_3(OH)_3$, and carbon dioxide. This compound, which is also known as *pyrogallic acid*, crystallizes in white needles which are exceedingly soluble in water. Its alkaline solution rapidly absorbs oxygen, becoming brown, and is therefore largely used in gas analysis. It is also employed in photography as a developer, as it reduces the salts of the noble metals. With ferric chloride it gives a red, with ferrous sulphate a blue coloration.

Tannic acid, $C_{14}H_{10}O_9$, is found together with gallic acid in gall-nuts, and other plants, and forms an amorphous powder, having a very astringent taste. It gives a bluish-black coloration with ferric chloride; and on boiling with dilute acids takes up the elements of water, forming two molecules of gallic acid, of which it is therefore a kind of anhydride. Its constitution is represented by the formula:



$$\left.\begin{array}{r} C_6H_2(OH)_3.CO \\ C_6H_2(OH)_2(CO_2H) \end{array}\right\rangle O.$$

AROMATIC COMPOUNDS WITH EIGHT ATOMS OF CARBON.

Dimethylbenzenes or *Xylenes*, $C_6H_4(CH_3)_2$.—Like other disubstitution products these exist in three modifications, corresponding to the dibromobenzenes. All three occur in coal-tar, but as they boil at about 140° they cannot be separated by fractional distillation. Each can however be obtained by synthesis. Thus *paraxylene* is obtained by acting on para-dibromobenzene with sodium and methyl iodide, and boils at 136°; *metaxylene* is formed by the distillation of mesitylenic acid, $C_6H_3(CO_2H)(CH_3)_2$, with lime, whilst *orthoxylene* is prepared from orthodibromobenzene in a similar manner to paraxylene.

The dibasic acids having the formula, $C_6H_4(CO_2H)_2$, are known as the *phthalic acids*. According to the theory three different phthalic acids should exist, and three have been obtained. They are distinguished as phthalic acid (1.2), isophthalic acid (1.3), and terephthalic acid (1.4), and are obtained by the oxidation of the xylenes and other benzenoid derivatives in which two atoms of hydrogen are replaced by alcohol radicals.

Phthalic Acid, $C_6H_4(CO_2H)$ (1.2), is obtained on the large scale by the oxidation of naphthalene, and crystallizes from hot water in large prisms. It melts at 185° and decomposes on distillation into *phthalic anhydride*, $C_6H_4(CO)_2O$, and water.

Isophthalic Acid, $C_6H_4(CO_2H)_2$ (1.3), crystallizes from hot water in thin slender needles, melts above 300°, and sublimes without decomposition.

Terephthalic Acid, $C_6H_4(CO_2H)_2$ (1.4) is a white powder, almost insoluble in water, and sublimes on heating without melting.

Ethylbenzene, $C_6H_5.C_2H_5$, is obtained by the action of sodium on a mixture of bromobenzene and ethyl bromide, and is a liquid boiling at 134°. By the action of bromine it yields the compound $C_6H_5.CH_2.CH_2Br$, which on treatment with alcoholic potash yields *styrolene* or *phenyl-ethylene*, $C_6H_5.CH{:}CH_2$, *i.e.* ethylene with one atom of hydrogen replaced by the phenyl group. Like ethylene itself this unites directly with bromine, forming the compound, $C_6H_5.CHBr.CH_2Br$, which on treatment with alcoholic potash yields *phenyl acetylene*, $C_6H_5C{:}CH$; this hydrocarbon like acetylene forms compounds with the metals such as $C_6H_5.C{:}CNa$.

AROMATIC COMPOUNDS WITH NINE ATOMS OF CARBON.

Trimethylbenzenes, $C_6H_3(CH_3)_3$.—Two compounds of this composition occur in tar-oil; one, termed *mesitylene*, boiling at 163°, can be prepared by heating acetone $CH_3.CO.CH_3$, with sulphuric acid, three molecules of this substance uniting with separation of water, just as three molecules of acetylene unite to form one of benzene; the methyl groups have the positions 1, 3, and 5. *Pseudo-cumene* (1, 3, 4, tri-methyl-benzene) boiling at 166° and *Cumene* (isopropyl benzene) boiling at 151°, are isomeric hydrocarbons.

Anethol, $C_6H_4.C_3H_5.OCH_3$, is the chief constituent of oil of anise. *Eugenol*, $C_6H_3(OH)(C_3H_5)(OCH_3)$, exists in oil of cloves and oil of pimento.

Cinnyl Alcohol, $C_6H_5.CH{:}CH.CH_2.OH$, is contained as cinnamic ether in liquid styrax, whilst *Cinnamaldehyde*, $C_6H_5.CH{:}CH.CHO$, is the chief constituent of the oil of cinnamon.

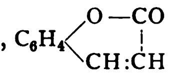
Cinnamic Acid, $C_6H_5.CH{:}CH.CO_2H$, exists in styrax, in balsams of Tolu and of Peru.

It may be prepared synthetically by heating benzaldehyde with sodium acetate and a dehydrating agent such as acetic anhydride :

$$C_6H_5.CHO + CH_3.CO_2Na = C_6H_5.CH{=}CH.CO_2Na + H_2O.$$

This reaction is very important, as many other aldehydes can be substituted for benzaldehyde, and homologues of cinnamic acid thus obtained. Cinnamic acid closely resembles benzoic acid, melts at 133°, and is converted by nascent hydrogen into *phenylpropionic acid*, $C_6H_5.CH_2.CH_2.CO_2H$, which crystallizes from water in long slender needles.

Coumarin,



$C_6H_4\left\langle\begin{matrix}O-CO\\ \vert\\ CH{:}CH\end{matrix}\right.$

is a crystalline solid found in the sweet woodruff, in Tonka bean, and in certain sweet-scented grasses. It can be artificially formed by acting on sodium-salicyl-aldehyde with acetic anhydride, and is the lactone of a hydroxycinnamic acid.

Tyrosin, $C_6H_4\left\{\begin{matrix}OH\\ C_2H_3(NH_2)CO_2H,\end{matrix}\right.$ is a product of the decomposition of albuminous bodies, hair, feathers, horn, &c. ; it likewise occurs in decomposing cheese, and in the cochineal insect.

AROMATIC COMPOUNDS WITH TEN TO TWELVE ATOMS OF CARBON.

Tetra-methyl-benzene, or *Durene*, $C_6H_2(CH_3)_4$, does not exist in coal-tar, but it can be artificially prepared by the action of sodium on a mixture of bromopseudocumene and methyl iodide ; it is a solid body melting at 79° and boiling at 190°.

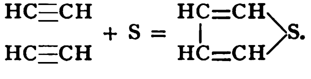
Methylisopropyl-benzene, or *Cymene*, $C_6H_4\left\{\begin{matrix}CH_3\\ C_3H_7\end{matrix}\right.$ is contained in Roman cummin-oil, and boils at 175°.

Thymol, $C_6H_3(OH)\left\{\begin{matrix}CH_3\\ C_3H_7,\end{matrix}\right.$ is contained in oil of thyme ; it forms tabular crystals, which melt at 44° and boil at 230°.

Mellitic Acid, $C_6(CO.OH)_6$, is contained as an aluminium salt in mellite, or honey-stone, which occurs in large octohedral crystals in the brown-coal formation.

THIOPHEN, C_4H_4S.

This compound occurs in small quantities in coal-tar benzene, and may be artificially prepared by passing acetylene through boiling sulphur :



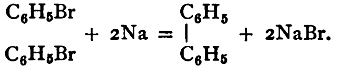
It boils at 84°, has the strongest possible resemblance both physically and chemically to benzene, and forms a series of derivatives which closely resemble those of benzene.

COMPOUNDS CONTAINING TWO OR THREE BENZENE NUCLEI.

We are acquainted with a large number of derivatives which contain two or more benzene nuclei, either combined together directly, as in the compound *Diphenyl*, $C_6H_5.C_6H_5$, or connected together by means of one or more intermediate carbon atoms, as with *diphenylmethane*, $C_6H_5.CH_2.C_6H_5$, *triphenylmethane*, $CH(C_6H_5)_3$, and *dibenzyl*, $C_6H_5.CH_2.CH_2.C_6H_5$.

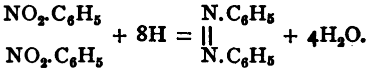
All these hydrocarbons give rise to a series of compounds similar to those described in the case of benzene. In this work it is impossible to do more than describe the more important derivatives.

Diphenyl, $C_{12}H_{10}$, is obtained, together with other substances, by passing benzene through a red-hot tube. It crystallizes in colourless peculiarly smelling plates, melts at 79·5° and boils at 240°. It is also prepared by acting on bromobenzene with sodium :



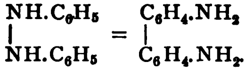
$$\begin{array}{l}C_6H_5Br\\ C_6H_5Br\end{array} + 2Na = \begin{array}{c}C_6H_5\\ |\\ C_6H_5\end{array} + 2NaBr.$$

Benzidine or *Diamidodiphenyl*, $(C_6H_4.NH_2)_2$.—Nitric acid acts on diphenyl in the same manner as on benzene, forming a nitro-compound, namely *p-dinitrodiphenyl*, $(C_6H_4.NO_2)_2$, which on reduction yields the corresponding diamido-compound, known as benzidine. It may also be readily prepared from nitrobenzene; this compound on reduction with zinc dust in alcoholic solution yields azobenzene.



$$\begin{array}{l} NO_2.C_6H_5 \\ NO_2.C_6H_5 \end{array} + 8H = \begin{array}{l} N.C_6H_5 \\ \| \\ N.C_6H_5 \end{array} + 4H_2O.$$

On further reduction azobenzene is converted into *hydrazobenzene*, $C_6H_5.NH.NH.C_6H_5$, which on treatment with mineral acids undergoes an intramolecular change forming the isomeric benzidine.



$$\begin{array}{l} NH.C_6H_5 \\ | \\ NH.C_6H_5 \end{array} = \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2. \end{array}$$

The latter crystallizes in large lustrous plates, and is manufactured on the large scale for the preparation of azo-colours similar to those already described (p. 404).

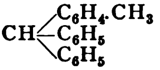
Triphenylmethane, $CH(C_6H_5)_3$, is formed by the action of chloroform on benzene in presence of aluminium chloride.

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

The manner in which the aluminium chloride acts is not known, but the reaction is a very general one and is largely used for preparing aromatic hydrocarbons. Triphenylmethane crystallizes from alcohol in lustrous plates, melting at 92°, and on oxidation yields an alcohol, *triphenylcarbinol*, $HO.C(C_6H_5)_3$, which crystallizes in hard six-sided prisms melting at 157°.

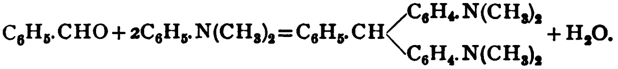
COLOURING-MATTERS DERIVED FROM TRIPHENYLMETHANE.

Triphenylmethane is the mother substance of a very important series of colouring matters, some of which are derived from triphenylmethane itself, and others from its *methyl* derivative, or *diphenyltolylmethane*.



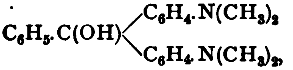
$$CH\begin{cases}C_6H_4.CH_3\\C_6H_5\\C_6H_5\end{cases}$$

Malachite-green is obtained by heating dimethylaniline with benzaldehyde and hydrochloric acid:



$$C_6H_5.CHO+2C_6H_5.N(CH_3)_2=C_6H_5.CH\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2\end{cases}+H_2O.$$

The *tetramethyldiamidotriphenylmethane* thus obtained is oxidized by lead dioxide to the corresponding carbinol,



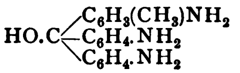
$$C_6H_5.C(OH)\begin{cases}C_6H_4.N(CH_3)_2\\C_6H_4.N(CH_3)_2,\end{cases}$$

which combines with acids with elimination of water and formation of malachite-green. The commercial product is the zinc double salt or the sulphate, and is used for dyeing wool, cotton, and silk green.

By the oxidation of mixtures of aniline and the toluidines two bases are obtained termed *pararosaniline*, $C_{19}H_{18}N_3(OH)$, and *rosaniline*, $C_{20}H_{20}N_3(OH)$. The first is formed from aniline and paratoluidine (solid), whilst aniline and liquid orthotoluidine yield rosaniline, the following equations representing the reactions:

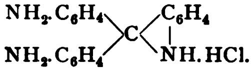
$$2C_6H_7N + C_7H_9N + 3O = C_{19}H_{19}N_3O + 2H_2O$$
$$C_6H_7N + 2C_7H_9N + 3O = C_{20}H_{21}N_3O + 2H_2O.$$

Pararosaniline can also be prepared from triphenylcarbinol in a way which shows its constitution. The latter compound is converted by nitric acid into a trinitro-derivative, $HO.C(C_6H_4.NO_2)_3$, and this on reduction yields, as usual, the corresponding amido-derivative, $HO.C(C_6H_4.NH_2)_3$, which is identical with pararosaniline. Rosaniline is the corresponding derivative of diphenyltolylmethane and has the constitutional formula:



$$HO.C\begin{cases}C_6H_3(CH_3)NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{cases}$$

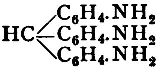
The free bases are colourless crystalline compounds, but combine with acids with elimination of water forming crystalline salts; these have a golden-green lustre and dissolve in water or alcohol, forming a beautiful red solution, which dyes fabrics the same colour. The hydrochloride of pararosaniline has the constitutional formula:



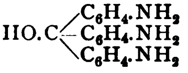
and on treatment with alkalis becomes colourless, the free base being reformed.

The commercial colouring matter known as *Magenta* or *Fuchsin* is a mixture of the salts of pararosaniline and rosaniline, obtained from a mixture of aniline and the two toluidines by oxidizing it with a mixture of nitrobenzene, iron, and hydrochloric acid.

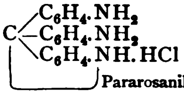
The coloured salts are converted by reducing agents into colourless substances known as *leucanilines* (λευκός, white). Thus pararosaniline hydrochloride yields *paraleucaniline*, which is found to be triamidotriphenylmethane. Of the three compounds



Leucaniline



Pararosaniline



Pararosaniline hydrochloride.

only the last is coloured, and the cause of the colour must, in some way, be due to the combination of the methane carbon atom with the nitrogen of the amido-group.

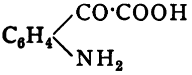
When rosaniline is heated with methyl alcohol and methyl chloride, the hydrogen of the amido-group is replaced partially or wholly by methyl, with formation of *Methyl-violets* or *Hofman's Violets*. The blue colour becomes more intense, the more methyl-groups the compound contains.

The *Paris violets* are obtained by oxidizing methyl- and dimethylaniline, and are also pararosaniline derivatives. Pure dimethylaniline yields pentamethylpararosaniline, the *hydrochloride* of which, $C_{19}H_{12}(CH_3)_5N_3.HCl$, forms crystals with a cupreous lustre, and dissolves in water with a deep violet-blue colour; on addition of a little sugar to the solution it forms a beautiful ink.

Hexamethylpararosaniline hydrochloride is very similar, a dark-blue powder. This, when evaporated to dryness and cut into small cakes, constitutes the indigo of commerce. The pure colouring matter termed *Indigotin* is obtained from commercial indigo in crystals by sublimation ; its composition is $C_{16}H_{10}N_2O_2$. Indigo is insoluble in water and in alcohol and ether ; strong or fuming sulphuric acid dissolves indigo, forming a deep-blue solution of indigotindisulphonic acid. Indigo occurs sometimes in healthy urine in small quantities. When indigo is exposed in contact with alkalis to reducing agents, it passes into a soluble and colourless substance by absorption of hydrogen. The substance thus produced is called *indigo white;* its formula is $C_{16}H_{12}N_2O_2$. This property is largely employed in indigo dyeing; an indigo vat is prepared, containing 1 part of indigo, 2 parts of ferrous sulphate, and 3 parts of slaked lime, to about 200 parts of water, these being allowed to stand together for some time in a closed vessel. The cloth is then dipped into the liquid, and on exposure to air becomes permanently dyed by the deposition of insoluble blue indigo in the fibre of the tissue.

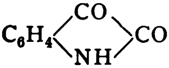
The constitution of indigo blue has been determined by a long series of researches, extending over many years, which have also brought to light a large number of interesting derivatives closely allied to it, and have rendered possible the synthetical production of the colouring matter.

By the oxidation of indigo it is converted into a yellow crystalline substance known as *isatin*, $C_8H_5NO_2$. This is also formed by heating ortho-amidophenylglyoxylic acid,



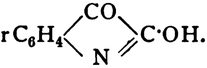
$C_6H_4\left\langle\begin{matrix}CO{\cdot}COOH\\ NH_2\end{matrix}\right.$

, and therefore has either the formula



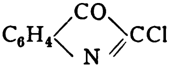
$C_6H_4\left\langle\begin{matrix}CO\\ NH\end{matrix}\right\rangle CO$

, or



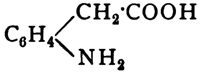
$C_6H_4\left\langle\begin{matrix}CO\\ N\end{matrix}\right\rangle C{\cdot}OH$

. As it yields a chloride of the formula



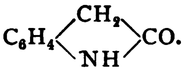
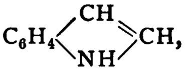
$C_6H_4\left\langle\begin{matrix}CO\\ N\end{matrix}\right\rangle CCl$

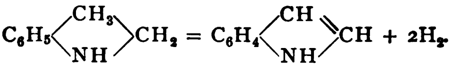
the latter is usually supposed to be correct. On further reduction isatin is converted into *Oxindole*, C_8H_7NO, which is also formed by heating ortho-amidophenylacetic acid.



$C_6H_4\left\langle\begin{matrix}CH_2{\cdot}COOH\\ NH_2\end{matrix}\right.$

, water being

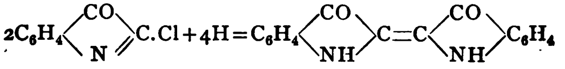
split off; it has therefore the constitution  $C_6H_4\left\langle\begin{matrix}CH_2\\NH\end{matrix}\right\rangle CO$.
On heating with zinc dust the latter substance is converted into a crystalline body termed *indole*,  $C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CH$, which is also obtained by passing the vapour of ethylaniline through a red-hot tube:



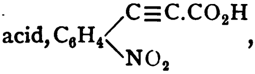
$$C_6H_5\left\langle\begin{matrix}CH_3\\NH\end{matrix}\right\rangle CH_2 = C_6H_4\left\langle\begin{matrix}CH\\NH\end{matrix}\right\rangle CH + 2H_2.$$

Indole is one of the products of pancreatic digestion, and also sometimes occurs in the urine.

Artificial Preparation of Indigo.—A number of different methods of obtaining indigo by synthesis have been discovered, but none have yet been so successful as to compete to any extent with the natural product. The one which throws the clearest light on the constitution of indigo is the reduction of isatin chloride (p. 422) with ammonium sulphide.



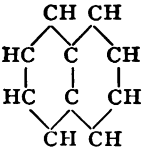
$$2C_6H_4\left\langle\begin{matrix}CO\\N\end{matrix}\right\rangle C.Cl + 4H = C_6H_4\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C = C\left\langle\begin{matrix}CO\\NH\end{matrix}\right\rangle C_6H_4 + 2HCl.$$

It is also formed by treating orthonitrophenylpropiolic acid,  $C_6H_4\left\langle\begin{matrix}C\equiv C.CO_2H\\NO_2\end{matrix}\right.$, with reducing agents, as well as by the action of fused caustic potash on monobromacetanilide, $C_6H_5.NH.CO.CH_2Br$, and on phenyl glycocoll, $C_6H_5.NH.CH_2.COOH$. The latter compound may also be directly converted into indigotindisulphonic acid by the action of fuming sulphuric acid.

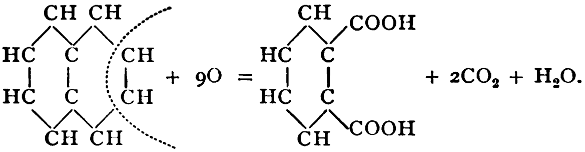
NAPHTHALENE GROUP.

Naphthalene, $C_{10}H_8$, is one of the chief constituents of coal-tar, and is formed in the dry distillation of many carbon compounds, especially when the distillate is heated to a very high temperature, being formed in this manner even from alcohol and acetic acid. It crystallizes in large pearly white plates, melts at 80°, boils at 217°, but sublimes at a lower temperature.

Naphthalene contains two benzene nuclei, which have two carbon atoms in common, as shown in the formula

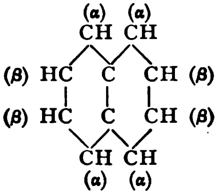


This is shown by the following considerations: when naphthalene is acted on by nitric acid, it yields nitronaphthalene, $C_{10}H_7NO_2$, which on oxidation forms nitrophthalic acid, showing the presence of at least one benzene nucleus. If nitrophthalic acid be reduced it yields amidonaphthalene, $C_{10}H_7NH_2$, and this on oxidation does not yield amidophthalic acid, but simply phthalic acid. Hence amidonaphthalene must also contain an unsubstituted benzene nucleus, as well as the one in which the amido-group is present, *i.e.*, naphthalene must contain two benzene nuclei. That the two carbon atoms common to both nuclei are adjacent to one another, as shown in the above formula, is proved by the fact that naphthalene is converted on oxidation into phthalic acid, $C_6H_4(CO_2H)_2$, in which as previously shown (p. 413) the carboxyl groups are attached to adjacent carbon atoms.



If the two common carbon atoms had not occupied the adjacent position, then by its oxidation either isophthalic acid, or terephthalic acid would be formed.

Naphthalene differs from benzene inasmuch as it forms two isomeric monosubstitution products, according as the *substituent* group is combined with a carbon atom which is in direct union with one of the common carbon atoms, or not. The two positions are designated *α* and *β*, as shown below.



Naphthalene yields halogen substitution products just in the same manner as benzene, but the number of possible isomerides is much larger, as no less than 10 isomeric disubstitution products can theoretically exist. The whole of the 10 dichloronaphthalenes have been prepared.

Two monohydroxy-derivatives of naphthalene exist, and are known as *α*- and *β-naphthol*, $C_{10}H_7(OH)$. They closely resemble phenol and are used in the preparation of colours. Thus the sodium compound of *α*-dinitronaphthol occurs in commerce as *naphthalene yellow*.

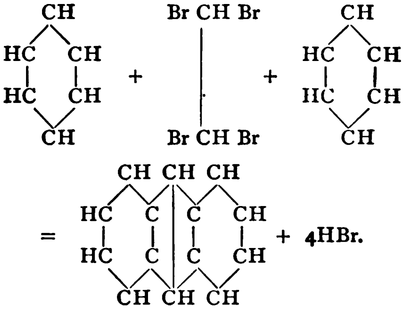
Similarly two amidonaphthalenes, $C_{10}H_7.NH_2$, corresponding to aniline are known, and are generally termed *α*- and *β-naphthylamine*. They yield diazo-compounds in the same manner as aniline, and these unite with other amido-compounds and phenols forming azo-colouring matters of great technical importance. One of these, *Biebrich scarlet*, is obtained from the sodium sulphonate of aniline yellow, $C_6H_4(SO_3H).N_2.C_6H_4.NH$ (also known as *Acid Yellow*), by converting it into a diazo-compound, and combining the latter with *β*-naphthol. It has the constitutional formula $C_{10}H_6(OH).N_2.C_6H_4\ N_2.C_6H_4.SO_3Na$. Again by the action of the diazo-compound of benzidine (p. 417) on *α*-amidonaphthalenesulphonic acid, we get *Congo red*, $C_{10}H_5(NH_2)SO_3Na.N_2.C_6H_4.C_6H_4.N_2C_{10}H_5(NH_2)SO_3Na$.

The corresponding compounds to benzoic acid, viz. *α*- and *β-naphthoic acid*, $C_{10}H_7,COOH$, show very analogous properties to that acid.

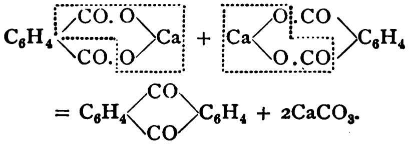
ANTHRACENE GROUP.

Anthracene, $C_{14}H_{10}$.—This hydrocarbon is contained in the least volatile portion of coal-tar oils, and crystallizes in white silky scales which have a pale blue fluorescence when quite pure; it melts at 213°, and boils above 360°.

It has been artificially prepared by the action of acetylene tetrabromide on benzene in presence of aluminium chloride, thus showing its constitution.

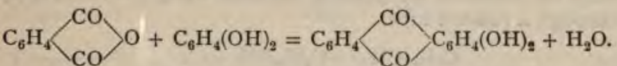


It yields substitution products with chlorine in the same manner as benzene and naphthalene. Its most important derivative is *anthraquinone*, $C_{14}H_8O_2$, which is readily formed by its oxidation. This substance forms yellow needles and has been prepared by synthesis in several ways; for example by heating calcium phthalate:



Its formation by the oxidation of anthracene is readily understood, the two central CH groups being oxidized to CO.

Alizarin, $C_{14}H_6O_2(OH)_2$, occurs as a glucoside (*ruberythric acid*) in the madder root; this undergoes decomposition into its constituents on boiling with acids or alkalis, or by a process of fermentation which goes on in the moist root. It is artificially prepared by sulphonating anthraquinone and fusing the sulphonic acid with caustic soda. It is a dihydroxyanthraquinone, as is also shown by its synthesis from phthalic anhydride and catechol.



$$C_6H_4\left\langle{CO \atop CO}\right\rangle O + C_6H_4(OH)_2 = C_6H_4\left\langle{CO \atop CO}\right\rangle C_6H_4(OH)_2 + H_2O.$$

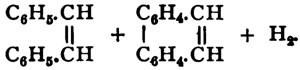
The commercial product obtained from anthraquinone-sulphonic acid is a mixture of various hydroxyanthraquinones, of which alizarin is the chief constituent.

This artificial production of alizarin is especially interesting as it is the first example (1868) of the synthesis of a naturally occurring vegetable colouring matter, and therefore marks an era in the history of applied chemistry.

Alizarin is deposited in long, red, needle-shaped crystals. It is but very slightly soluble in cold, but more soluble in hot water, and easily dissolves in alcohol. Alizarin produces insoluble red-coloured compounds with alumina and stannic oxide, which are termed lakes, and a purple or black compound with ferric oxide. Hence in calico-printing, solutions of these oxides are used as *mordants*, and are printed in pattern on the cotton cloth, which after undergoing certain preparatory processes, was formerly boiled in the "dye-beck," containing the ground madder-root mixed with water. The alizarin of the madder forms with the mordanted cloth an insoluble compound, which is coloured pink, purple, black, or chocolate, according as the mordant has been pure alumina or pure iron, or a mixture of the two. Since the introduction of artificial alizarin the use of madder-root has been entirely discontinued and the processes of dyeing and calico-printing thereby much simplified. The so-called Turkey-red cloth is cotton cloth, first mordanted with oil and alumina, and afterwards dyed with alizarin. Animal fabrics, such as silk or wool, do not require the application of mordants; they are able alone to fix and render insoluble the colouring matter.

The madder-root yields another red-colouring matter, termed *Purpurin*, which is a trihydroxyanthraquinone; an isomeric compound known as *Anthrapurpurin* is contained in crude artificial alizarin, and behaves towards mordants in the same manner as alizarin, but gives a brighter red colour.

Phenanthrene, $C_{14}H_{10}$.—This hydrocarbon, which is isomeric with anthracene, is also contained in coal-tar; it may be obtained by passing stilbene $C_6H_5.CH : CH.C_6H_5$ through a red-hot tube.



$$\begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} + \begin{array}{l} C_6H_4.CH \\ |\qquad \| \\ C_6H_4.CH \end{array} + H_2.$$

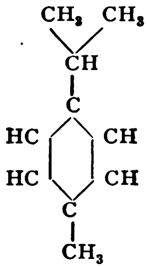
It crystallizes in plates, melts at 100°, and boils at 340°.

LESSON XL

THE TERPENES, CAMPHOR, AND THE GLUCOSIDES

UNDER the general name of Terpenes is included a series of closely related hydrocarbons having the formula $C_{10}H_{16}$. They occur in the ethereal oils obtained chiefly from the conifers and different varieties of *Citrus*. A very large number of isomerides have been described, but more accurate investigation has shown that many of these are mixtures. At present nine distinct compounds of this formula are known, viz.: Pinene, Camphene, Fenchene, Limonene, Dipentene, Sylvestrene, Phellandrene, Terpinene, and Terpinolene.

These stand in very close relation to one another, and also to the aromatic hydrocarbon Cymene, $C_{10}H_{14}$ (p. 415), which is paramethylisopropyl benzene.



They mostly combine with one or two molecules of bromine or hydrogen chloride, and also form very characteristic additive compounds with nitrosyl chloride, NOCl. They readily lose two atoms of hydrogen forming cymene, and yield paratoluic acid and terephthalic acid on oxidation, and must therefore be regarded as additive benzene derivatives, *i.e.* as dihydrocymenes.

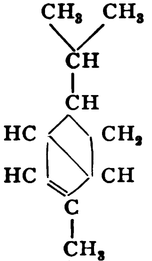
Pinene, $C_{10}H_{16}$, is the chief constituent of common oil of turpentine, which is obtained from the ethereal oil of different conifers by distilling with steam, rosin, or colophony remaining behind. It also occurs in varying quantity in numerous other ethereal oils. Oil of turpentine is a colourless liquid, which has a very characteristic odour, boils at 158-160°, and has a specific gravity of 0·856-0·87. It is almost insoluble in water, but is miscible with alcohol and ether, and dissolves sulphur, phosphorus, resins and caoutchouc, and is therefore used in the preparation of varnishes and oil paints. The oil of turpentine from various sources has a different specific rotatory power, owing to the fact that its chief constituent, pinene, exists in two optically isomeric forms, viz., dextro- and laevo-pinene. The so-called French and German oils (from *Pinus sylvestris* and *maritima*) are laevorotatory and the English variety (from *P. australis*) is dextrorotatory. The oil gradually absorbs oxygen from the air, becoming resinous, and is oxidized by nitric acid to various fatty acids, terebic acid, toluic acid, terephthalic acid, &c.

Pinene combines with one molecule only of chlorine and bromine, forming oily additive compounds which readily decompose on heating into hydrochloric or hydrobromic acid and cymene. *Pinene hydrochloride*, $C_{10}H_{17}Cl$, obtained by the action of dry hydrogen chloride on pinene, is a crystalline compound, which smells like camphor and is sometimes known as *artificial camphor.* It behaves as a saturated compound.

Pinene nitroso-chloride, $C_{10}H_{16}(NO)Cl$, is obtained by the action of nitrosyl chloride, or a mixture of amyl nitrite, acetic and hydrochloric acids on pinene. It melts at 103°, and readily loses its chlorine by double decomposition with fatty amines or piperidine-forming compounds known as *nitrolamines*. Thus piperidine yields the compound $C_{10}H_{16}(NO).NC_5H_{10}$.

Pinol or *Sobrerol*, $C_{10}H_{16}O$, a substance isomeric with camphor, is obtained as a by-product in the preparation of pinene nitrosochloride from amyl nitrite, and is also formed by the oxidation of oil of turpentine in the sunlight.

From the above reactions it appears that pinene contains only one ethylene linkage, and two of the carbon atoms in the para-position are probably linked together, as shown in the following formula :



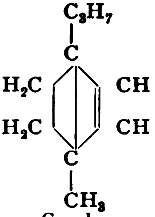
Pinene.

Camphene is obtained from pinene hydrochloride by eliminating hydrogen chloride or from camphor by reducing it to borneol, $C_{10}H_{18}O$ (see below), and treating the latter with a dehydrating agent.

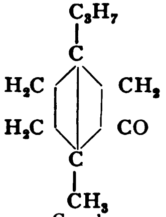
Camphor, $C_{10}H_{16}O$, is found in the camphor tree (*Laurus camphora*), indigenous to China and Japan, together with laevopinene and dipentene. It forms a crystalline transparent mass, which has a very characteristic odour, melts at 175°, and boils at 204°. It is oxidized by nitric acid to the dibasic *camphoric acid*, $C_{10}H_{16}O_4$. Camphor exists in two optically isomeric forms, and unites with hydroxylamine and phenylhydrazine with elimination of water, and therefore contains a carbonyl group.

Borneol, Bornyl alcohol or *Borneo-camphor*, $C_{10}H_{16}O$, is found in *Dryobalanops camphora*, a tree indigenous to Borneo and Sumatra. It is also obtained by reducing camphor with sodium in alcoholic solution. It melts at 206°, boils at 212°, and has a smell resembling that of camphor and pepper.

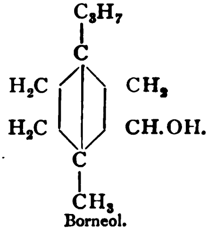
The constitution of these three compounds is probably as follows:



Camphene.

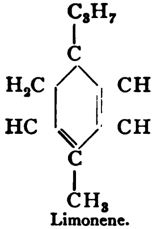


Camphor.



Borneol.

Fenchene is obtained from *Fenchone*, $C_{10}H_{16}O$, a compound contained in fennel, and is very closely allied in its properties to camphor. *Dextro-limonene* or *Citrene* is found in the ethereal oil obtained from oranges and lemons. The laevo-rotatory modification is obtained from *Pinus sylvestris*. Both are pleasant-smelling liquids of specific gravity 0·846 at 20°, and boil at 175-176°. They combine with two molecules of chlorine and bromine and therefore contain two ethylene linkages. The most probable formula is



Limonene.

Dipentene is the most stable of the terpenes and is obtained from pinene, camphene and limonene by heating them at 250-300°. It also occurs in wormseed oil together with cineol, and is a pleasant-smelling liquid which boils at 175-176°, has a specific gravity of 0·853, and is optically inactive. It is in fact *inactive limonene*, and may be obtained by mixing equal parts of dextro- and laevo-limonene.

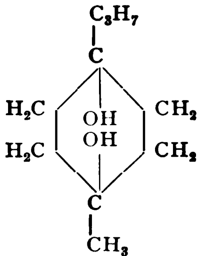
Dipentenylene dichloride, $C_{10}H_{18}Cl_2$, is formed by the action of an acetic acid solution of hydrogen chloride on limonene or dipentene, or of fuming hydrochloric acid on oil of turpentine. It crystallizes in rhombic tablets, melting at 50°.

Dipentenylene glycol or *Terpinol*, $C_{10}H_{18}(OH)_2+H_2O$, is formed by the action of alcohol on the chloride, or by allowing a mixture of turpentine, nitric acid and alcohol to stand. It crystallizes in large transparent prisms, which lose their water of crystallization on heating, then melt at 102° and boil at 258° without decomposition.

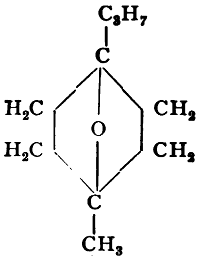
Dipentenylene oxide or *Cineol*, $C_{10}H_{18}O$, is the chief constituent of wormseed oil, and occurs also in rosemary oil and eucalyptus oil. It is a pleasant-smelling liquid, which boils at 176°, and is optically inactive.

Terpineol, $C_{10}H_{17}OH$, is formed by boiling the above glycol with dilute phosphoric acid, and is also found in Cardamom oil. It is also a pleasant-smelling liquid.

The constitution of terpinol and cineol is probably as follows:



Terpinol.



Cineol.

RESINS AND BALSAMS.

Most of the ethereal oils are converted by absorption of oxygen into more or less solid compounds; these are termed *resins*, or if they still contain unaltered ethereal oils, *balsams.* Thus *rosin* or *colophony* is obtained in the preparation of oil of turpentine; the other resins, such as lac, mastic and copal are very similar.

CAOUTCHOUC AND GUTTA-PERCHA.

These substances are hydrocarbons which have the same composition as the terpenes, but scarcely anything is known of their chemical properties. Caoutchouc or india-rubber, is the hardened milk sap of several tropical trees, (*Ficus elastica*, *Jatropha elastica*, *Siphonia Cahuchu*, &c.,) and in the pure state is white and transparent. It is insoluble in water, but swells up and finally dissolves in carbon bisulphide and in oil of turpentine. Caoutchouc is largely employed for the preparation of waterproof articles, elastic tubes, &c. &c., and is of great importance to the chemist. It combines with sulphur in different proportions (the process being known as *vulcanization*) yielding substances which have very valuable properties. Thus a substance containing 2–3 per cent. of sulphur is much more elastic than the unvulcanized substance, whilst a larger quantity converts it into a hard horn-like mass, known as *ebonite* or *vulcanite*, which is employed instead of horn for the manufacture of combs and similar articles.

Gutta-percha is the dried milk sap of *Isonandra Gutta*, a tree which is frequently found in the Malay peninsula. At the ordinary temperature it is hard and brittle, but becomes plastic on warming and may then be moulded to any form. The pure substance is white, and readily soluble in chloroform and carbon bisulphide.

GLUCOSIDES.

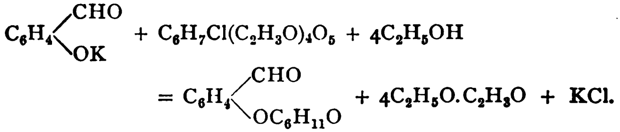
The numerous substances constituting this class occur in the bodies of many plants, and yield a glucose on decomposition, together with other bodies; they may be considered as compound ethers of glucose. Amygdalin and salicin may serve as examples of this class of compounds.

Amygdalin, $C_{20}H_{27}NO_{11} + 3H_2O$, is found in bitter almonds, and obtained by extraction with alcohol, and precipitation with ether ; it forms small white crystals which are soluble in water. The most remarkable decomposition which amygdalin undergoes is that which is brought about in the bruised almond by the presence of an albuminous substance called ***emulsin*** or *synaptase*, by which bitter almond oil, hydrocyanic acid, and glucose are produced :

$$\overset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2H_2O = \overset{\text{Benzaldehyde.}}{C_7H_6O} + \overset{\text{Hydrocyanic Acid.}}{HCN} + \overset{\text{Glucose.}}{2C_6H_{12}O_6}.$$

Salicin, $C_{13}H_{18}O_7$, is contained in the pith of the willow and poplar, and also found in the castoreum contained in a gland of the beaver. Salicin crystallizes in bright white needles, is soluble in water and alcohol, but insoluble in ether ; its solution possesses a strongly bitter taste. In presence of certain ferments it is decomposed with formation of glucose and saligenin or orthohydroxybenzylalcohol (p. 411).

On oxidation salicin is converted into ***helicin***, the glucoside of salicylaldehyde, $C_6H_4(CHO)OC_6H_{11}O_5$. which crystallizes in small needles and has been artificially prepared. When glucose is acted upon with acetyl chloride it yields acetochloroglucose, $C_6H_7Cl(C_2H_3O)_4O_5$, and this on treatment with the potassium compound of salicylaldehyde in alcoholic solution yields helicin :



$$C_6H_4\begin{cases}CHO\\OK\end{cases} + C_6H_7Cl(C_2H_3O)_4O_5 + 4C_2H_5OH$$
$$= C_6H_4\begin{cases}CHO\\OC_6H_{11}O\end{cases} + 4C_2H_5O.C_2H_3O + KCl.$$

As helicin is converted into salicin by the action of sodium amalgam in water, that compound can also be artificially prepared.

Myronic Acid, $C_{10}H_{16}NS_2O_{10}$.—The potassium salt of this acid exists in the seeds of black mustard : it decomposes into oil of mustard (allyl-thiocarbimide), glucose, and hydrogen potassium sulphate, in contact with an albuminous ferment found in the seeds :

$$\overset{\text{Potassium Myronate.}}{C_{10}H_{18}KNS_2O_{10}} = KHSO_4 + \overset{\text{Oil of Mustard.}}{C_3H_5N.CS} + \overset{\text{Glucose.}}{C_6H_{12}O_6}.$$

Indican, $C_{52}H_{62}N_2O_{34}$, is a glucoside of indigo; and *Ruberythric acid*, $C_{26}H_{28}O_{14}$, is a glucoside contained in madder-root, which yields alizarin.

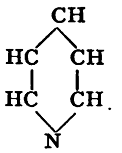
Coniferin, $C_{16}H_{22}O_8$, is a glucoside obtained from the cambium of coniferous trees. This when heated with water and emulsin splits up into glucose and a crystalline body $C_{10}H_{12}O_3$, which on oxidation yields *vanillin*, $C_8H_8O_3$, the odoriferous component of vanilla-root. (p 412).

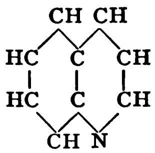
LESSON XLI

THE ALKALOIDS

THIS name is given to a class of basic compounds containing carbon, hydrogen, nitrogen, and often oxygen, which occur in many plants. They combine with acids, and as a rule yield well crystallized double salts with platinum chloride. Many of them, such as strychnine and nicotine, are extremely violent poisons, whilst others, such as morphine and quinine, are most valuable drugs.

The exact constitution of only a few of these has been settled, but they all contain a closed chain of carbon and nitrogen atoms, most of them being derived from two nitrogenous bases, termed pyridine and quinoline, which may be regarded as benzene and naphthalene in which one CH group has been replaced by an atom of nitrogen, as shown in the following formulæ:


Pyridine.

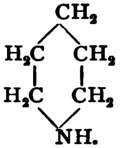

Quinoline.

These two compounds give rise to a large number of derivatives similar to those of benzene and naphthalene, some of which have proved to be identical with naturally occurring alkaloids.

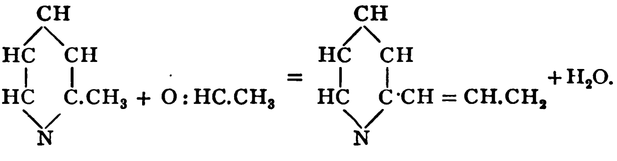
Pyridine occurs in the oil obtained in the dry distillation of bones. It is a liquid, having a very penetrating odour, and boils at 114·5. *Quinoline* occurs in coal tar, and is also formed by distilling quinine, cinchonine, &c. with potash ; it is a peculiar smelling liquid and boils at 238°.

Pyridine and quinoline form additive compounds with hydrogen much more readily than the corresponding benzene compounds. The former on reduction yields

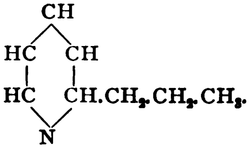
Piperidine, $C_5H_{10}NH$, which is also obtained by distilling piperine, the base contained in black pepper with an alkali. It is a colourless liquid, which boils at 106°, and has an odour resembling that of pepper and ammonia. Its constitution is represented by the formula :



Coniine, $C_8H_{17}N$ is contained in the seeds of the hemlock (*Conium Maculatum*). It is a colourless very poisonous liquid, which boils at 168°, has a strong alkaline reaction, and forms salts with acids. It has been obtained synthetically from pyridine in the following manner. When pyridine is treated with methyl iodide it yields *a-methylpyridine* or *picoline*, $C_5H_4(CH_3)N$, which on treatment with aldehyde yields *allylpyridine*:



On addition of sodium to the boiling alcoholic solution of the latter it takes up 8 atoms of hydrogen forming propylpiperidine



which has all the properties of coniine, with the exception that it has no action on the plane of polarized light, whilst the natural coniine rotates the plane to the right. If the artificial base is converted into the tartrate, however, it may be separated into a more soluble and less soluble portion. The free base precipitated from the latter is in all respects identical with the natural product, whilst the base obtained from the more readily soluble tartrate, differs from it only in rotating the plane of polarization to the left.

Nicotine, $(C_5H_7)_2N_2$, is the chief alkaloid of tobacco, which contains varying quantities, from 2 to 8 per cent. of this substance. Nicotine boils at about 246°, undergoing partial decomposition, but it may be distilled in an atmosphere of hydrogen without change.

Nicotine is soluble in water, alcohol, and ether, and acts as one of the most violent poisons with which we are acquainted: a small quantity acting on the motor nerves, and producing convulsions and afterwards paralysis. Nicotine does not contain any hydrogen replaceable by an alcohol radical, and, when treated with iodide of ethyl, yields a salt corresponding to ammonium iodide:

$$(C_5H_7)_2N_2 + 2C_2H_5I = (C_5H_7)_2(C_2H_5)_2N_2I_2.$$

Alkaloids containing Carbon, Hydrogen, Oxygen, and Nitrogen.

Alkaloids of Opium.—Opium is the dried juice of the head of the poppy (*Papaver somniferum*); it is prepared largely in Asia Minor, Turkey, Egypt, and India. The Smyrna opium is most esteemed, and contains from 10 to 15 per cent. of morphine. There are no less than fifteen different alkaloids contained in opium, of which morphine and narcotine are found in largest quantity. The most important are:

Morphine	$C_{17}H_{19}NO_3$.	Papaverine	$C_{21}H_{21}NO_4$.
Codeine	$C_{18}H_{21}NO_3$.	Narcotine	$C_{22}H_{23}NO_7$.
Thebaine	$C_{19}H_{21}NO_3$.	Narceine	$C_{23}H_{29}NO_9$.

In addition to these substances, opium contains a neutral crystallizable substance called Meconine, $C_{10}H_{10}O_4$, and an acid called Meconic Acid, $C_7H_4O_7$, with which the alkaloids are chiefly combined, as well as many other substances in small quantities, besides extractive matter, &c. Opium serves as a most valuable medicine, acting in small doses as a sedative, although heightening the pulse and the action of the heart. Taken in larger doses it acts as a narcotic poison, a stupor and prostration soon ensuing, resulting in loss of all voluntary power of motion, complete coma, and death. It appears that thebaine is the most powerful of the alkaloids, then narceine, papaverine, codeine, morphine, and narcotine.

Morphine, $C_{17}H_{19}NO_3+H_2O$.—In order to prepare morphine, the opium is extracted with water, and the meconic acid precipitated by calcium chloride; on evaporating the filtrate, crystals of morphine hydrochloride separate out. Morphine dissolves in 1,000 parts of cold and 500 of boiling water: hot alcohol dissolves it easily, whilst it is insoluble in ether. It forms crystalline salts soluble in water, and contains no replaceable hydrogen, an ammonium iodide being obtained when it is acted upon with ethyl iodide. Small quantities of morphine can easily be detected by the formation of a deep-blue coloration when this substance comes in contact with ferric chloride.

Apomorphine, $C_{17}H_{17}NO_2$, is obtained by heating morphine under pressure with hydrochloric acid. Its salts produce vomiting when given in small doses.

Codeine, or *Methyl-morphine*, $C_{17}H_{18}(CH_3)NO_3+H_2O$, is left in the mother-liquors from which the morphine has crystallized out. Codeine is much more soluble in water than morphine, and is contained in opium in much smaller quantities; it has a strong alkaline reaction, and neutralizes acids.

When codeine is heated with hydrochloric acid under pressure, apomorphine and methyl chloride are formed.

Thebaine, $C_{19}H_{21}NO_3$, is contained in very small quantities in opium: its poisonous properties are more violent than any other of these alkaloids: it produces tetanus.

Papaverine, $C_{21}H_{21}NO_4$, is distinguished from the other opium bases by giving a deep-blue colour with strong sulphuric acid.

Narcotine, $C_{22}H_{23}NO_7$, remains insoluble when opium is treated with water, and it is obtained by dissolving it out from the "marc" or insoluble portion of the opium, with acetic acid. It dissolves in 128 parts of boiling alcohol and 19 of boiling ether. Narcotine when heated with potash furnishes ammonia and methylamine, as well as di- and trimethylamine; and when treated with hydriodic acid, it furnishes 3 molecules of methyl iodide, and 1 molecule of a new base called nornarcotine for every molecule of narcotine:

$$C_{19}H_{14}(CH_3)_3NO_7 + 3HI = C_{19}H_{17}NO_7 + 3CH_3I.$$

Alkaloids of the Strychnos.

Two alkaloids possessing most powerful poisonous properties, and called Strychnine and Brucine, are found in the seeds of the *Strychnos Nux Vomica* and in the *Strychnos Ignatius*, or St. Ignatius's bean.

Strychnine, $C_{21}H_{22}N_2O_2$, is a base forming crystallizable salts, of which 1·5 per cent. is contained in St. Ignatius's bean. It acts as a violent poison, producing tetanic convulsions: it is however sometimes given in very small doses in medicine. Its salts are all extremely bitter and tart. Strychnine can be detected, when present in the minutest quantities, by its yielding with sulphuric acid and potassium bichromate an intense purple colour, which passes rapidly into red, and then into yellow.

Brucine, $C_{23}H_{26}N_2O_4 + 4H_2O$, is found alone in false angustura bark, and together with strychnine in *Nux Vomica*, it is more soluble in water than alcohol and strychnine. Brucine and its salts are less poisonous and less bitter than the strychnine compounds. It can be distinguished from strychnine by the bright red colour produced when it is moistened with nitric acid; indeed this reaction may also be employed as a most delicate test for the presence of nitric acid.

Curarine, $C_{10}H_{15}N$, is a peculiar alkaloid contained in the curare arrow-poison; it acts as a most powerful poison.

Alkaloids of the Cinchonas.

The bark of this species of trees, originally known in Peru, but now transplanted to Java and India, contains two alkaloids, quinine and cinchonine: and each of these yields two isomeric modifications, quinidine and quinicine, cinchonidine and cinchonicine.

The alkaloids are combined in the bark with a peculiar acid termed *quinic acid*, $C_6H_7(OH)_4.CO_2H$. Quinine is a most valuable medicine, acting as a febrifuge; cinchonine does not possess the same valuable properties.

Quinine, $C_{20}H_{24}N_2O_2$.—This alkaloid may be precipitated from the solution of its sulphate as a white crystalline powder. It dissolves in 900 parts of cold water, and in 2 parts of alcohol. Its solution has a strong bitter taste, and rotates the plane of polarization to the *left*. Quinine may be detected by adding chlorine water, and afterwards an excess of ammonia, to solutions of the sulphate, when a green colour is produced. Another characteristic reaction consists in the deep red colour produced when finely powdered potassium ferrocyanide is thrown into the solution of quinine in chlorine water. Quinine possesses no replaceable hydrogen, as when treated with ethyl iodide a salt of an ammonium compound is formed. Quinine sulphate is the salt used in medicine; it is not very soluble in water, but dissolves easily when a drop or two of sulphuric acid is added. Its solution possesses very strongly the property of *fluorescence*.

Quinidine and Quinicine.—The first of these isomerides of quinine is found in the bark, and it resembles quinine in its febrifuge qualities, but rotates the plane of polarization strongly to the *right*. Quinicine is obtained by acting upon quinine by heat. It is a bitter substance, possessing a semi-solid resinous consistency, and rotating the plane of polarization feebly to the right.

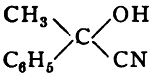
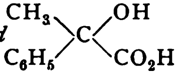
Cinchonine, $C_{20}H_{24}N_2O$.—This body is separated from the quinine which accompanies it by means of its lesser solubility in alcohol : thus cinchonine requires 30 parts of boiling alcohol for solution, and therefore crystallizes out whilst the quinine remains in solution. Cinchonine is not nearly so powerful a febrifuge as quinine ; it is, however, used as a medicine in some countries. Although it only differs from quinine by containing one atom less oxygen, it has not yet been transformed into the latter. It does not produce a green colour with chlorine water and ammonia like quinine ; it acts as a strong base, and forms salts which are more soluble in water and alcohol than those of quinine.

Cinchonidine—Cinchonicine—The first of these isomerides is found, together with quinidine, in the brown resinous mass left after the extraction of the two chief alkaloids. It rotates the plane of polarization to the left, whilst cinchonine has a dextro-rotatory action. Cinchonicine is obtained by heating a cinchonine sulphate to 120° or 130° ; it rotates the plane of polarization feebly to the right. Hence we have

Quinine	exerting a	powerful left-handed	rotation.
Quinidine	,,	powerful right-handed	,,
Quinicine	,,	feeble right-handed	,,
Cinchonine	,,	powerful right-handed	,,
Cinchonidine	,,	powerful left-handed	,,
Cinchonicine	,,	feeble right-handed	,,

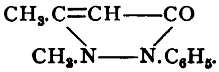
Solanum Alkaloids.—These plants contain an alkaloid $C_{17}H_{23}NO_3$, occurring in three isomeric forms, each of which exerts in a remarkable degree the power of enlarging the pupil of the eye. These are termed *Atropine*, found in *Atropa belladonna ; Hyoscyamine*, in the *Hyoscyamus niger ;* and *Hyoscine.*

When these three substances are treated with hydrochloric acid, they are converted into isomeric bases of the formula $C_8H_{15}NO$, and an acid known as *tropic acid*, $C_9H_{10}O_3$. The latter is also obtained by acting on methylphenylketone, $CH_3.CO.C_6H_5$ with hydrocyanic acid, and treating the nitrile

 thus formed with hydrochloric acid. It is therefore *a-phenyllactic acid* 

Cocaïne, $C_{17}H_{21}NO_4$ is found in coca-leaves,and is employed in surgery for producing local anaesthesia, especially in operations on the eye.

Antipyrine, $C_{11}H_{21}N_2O$. This important compound, now so largely employed as a medicine, somewhat resembles the alkaloids, and derives its name from its power of lowering the temperature of the animal body. It is obtained by acting with phenylhydrazine, $C_6H_5.NH.NH_2$ on acetoacetic ether, $CH_3.CO.CH_2.CO_2C_2H_5$, and treating the product with methyl iodide. It has the constitution



LESSON XLII

ALBUMINOUS SUBSTANCES

UNDER this head we class a number of peculiar compounds of very complicated constitution, of whose true chemical relations we are yet very ignorant. They do not crystallize, and exist in an amorphous jelly-like form : hence it is difficult to obtain them in the pure state, and it is therefore almost impossible to ascertain with exactness their chemical composition, still less their constitution. They all contain sulphur, in addition to carbon, hydrogen, oxygen, and nitrogen, and in their different forms possess nearly, although by no means precisely, the same composition.

The albuminous substances are primarily built up by plants, from the very simple chemical compounds which constitute their food, and are stored up in larger or smaller quantities in the tissues and organs of the plant, some of which, such as the seeds, often contain them abundantly.

Even in the same plant the albuminous substances differ in chemical reactions, in chemical composition, and in physical characters.

From the plant exclusively the animal derives its supplies of the albuminous substances which constitute by far the greater part of the solids of its body. Whatever the variety of albuminous substance upon which it feeds, the animal possesses the power of converting it into the special albuminous compounds which are characteristic of its various tissues and fluids. Animals which are vegetable feeders obviously derive the albuminous substances of their tissues *directly* from vegetables. Carnivorous animals do so *indirectly*, for, living upon the bodies of the vegetable feeders, they obtain the stores of albuminous substances which these have previously derived from plants.

Albumin, properly so called, exists in many of the solids and fluids of the animal body. It occurs in its purest form in the white of egg, and in the serous or liquid portion of the blood. It may be obtained from white of egg, by beating it up, diluting with water, and filtering the solution which is thus obtained to free it from the shreds of membrane with which it is mixed. The fluid, which is slightly alkaline, may be neutralised with acetic acid and then evaporated at a very gentle heat. An amorphous, yellowish, transparent, gum-like mass is thus obtained, which is soluble in cold water.

One of the most characteristic properties of a solution of albumin is its power of coagulation. If a solution of white of egg, or of albumin prepared from it, be heated to about 70°, it becomes solid and opaque ; in this state it is insoluble in water, but dissolves in dilute alkalis. Solutions of albumin are also precipitated by the strong mineral acids, specially by nitric acid, and by solutions of various metallic salts, as for instance corrosive sublimate and lead acetate.

Alkaline albuminates are formed by the action of solutions of the alkalis upon the various albuminous bodies. They are compounds of the alkali-metal used with albumin. Albuminate of potassium is readily formed by beating up the white of egg and then adding a solution of caustic potash drop by drop to the fluid, with continual stirring. A very viscid, yellow, transparent mass is thus formed, which may be freed from excess of alkali by washing with water. The alkaline albuminates are all soluble in water; their solutions are not coagulated by heat, and when neutralised by the addition of an acid, a precipitate of insoluble albumin is thrown down.

Albumin is converted by the action of dilute acids into a body called *syntonin*, or *acid albumin*. All the albuminous bodies appear capable of furnishing syntonin; if muscle, for instance, be digested for a day or two in dilute hydrochloric acid, it swells up and almost completely dissolves, and the solution contains syntonin. Solutions of syntonin are not coagulated by heat. When neutralised by alkalis, albumin is thrown down.

Fibrin.—This substance does not exist pre-formed in blood, but separates from it in a solid state almost immediately after it has left the body. It may be readily obtained by stirring blood, as it flows from the vessels of a living animal, with twigs. After some minutes a white stringy substance is found adhering to the twigs. By washing with water this may be obtained as a greyish-white or white, stringy, elastic solid. Fibrin is tasteless, insoluble in water, and, on drying, forms a heavy mass, like albumin.

It is now well ascertained that fibrin is produced from the blood by the interaction of two albuminous bodies, which exist in solution in the *liquor sanguinis*; *i.e.* in the fluid in which the blood corpuscles float. These albuminous substances are called fibrinogen and fibrinoplastic substance. The immediate cause of their combination to form fibrin appears to be a *ferment* which is readily formed in blood after it has left the body, and which is called the fibrin-ferment. When blood is not stirred after it has been drawn from the body, it coagulates in a period which varies from one to several minutes, *i.e.* it becomes converted into a solid jelly. After some hours this jelly contracts somewhat, and an almost colourless, sometimes slightly opalescent fluid, separates from it. The jelly is called the *clot*, the fluid the *serum*. The former consists of fibrin which has solidified and entangled within its meshes the blood corpuscles; the latter is the *liquor sanguinis*, from which the fibrin generators, above referred to, have separated.

Casein is the albuminous substance contained in milk and cheese. It is now recognized to be an alkaline albuminate.

In milk, the casein is not coagulated by boiling, but an acid, or a portion of the inner coating of the calf's stomach, called *rennet*, at once separates out the casein and butter as *curds*, and leaves the milk, sugar, and salts in solution as *whey*.

Globulin is the albuminous constituent of the crystalline lens of the eye. In chemical reactions it resembles closely the fibrin generators, fibrinogen and fibrinoplastic substance. It is precipitated from its solutions by carbonic acid, or by the addition of common salt.

Myosin is an albuminous body which exists in solution in the living juice of muscle, but which coagulates at death.

Vegetables, as we previously remarked, contain substances similar to the albuminous bodies of animals, and from which indeed the latter are all, more or less directly, derived.

Glutin is a sticky, elastic substance, which, when fresh and moist, can be drawn out into threads; it is a mixture of various vegetable albuminous substances, which exist with starch in wheaten flour; the principal of these are *gliadin* and *vegetable fibrin*. Vegetable albumin and casein occur in the juices and seeds of plants.

The limits of the variation in chemical composition of the different albuminous compounds is found to be as follows:

Percentage of	carbon	52·7 to 54·5
,,	hydrogen . . .	6·9 to 7·3
,,	nitrogen . . .	15·4 to 16·5
,,	sulphur	0·8 to 1·6
,,	oxygen	20·9 to 23·5

Hence we see that it is not at present possible to represent these complicated compounds by any chemical formulæ.

Gelatin is a nitrogenous substance obtained from the animal body, probably somewhat closely connected with the albuminous substances. It is obtained by boiling for a long time the so-called connective tissues of the body, or organs rich in connective tissue, as the tendons, ligaments, bones and skin. It does not exist pre-formed in the tissues, being only obtained from them by the prolonged action of boiling water, or by the action of superheated steam.

Animal Chemistry is a most important branch of chemical science, and one which unfortunately is but very slightly advanced: our knowledge of the composition and chemical constitution of the substances contained in the animal body is very incomplete, and concerning many of the chemical changes which occur in the different parts of the animal we are almost entirely ignorant.

The *Bones* of animals consist principally of tribasic calcium phosphate, deposited in an organic basis; the latter is composed of a substance which on prolonged boiling yields gelatin; the earthy phosphate dissolves in hydrochloric acid, leaving the bone as an elastic gelatinous mass. When burnt, the friable and earthy matter alone remains. Bone contains:

Animal matter	33
Calcium triphosphate	57
Calcium carbonate	8
Calcium fluoride	1
Magnesium phosphate	1
	100

The *Blood* of animals is the channel by means of which their bodies not only receive all the requisite supply of materials for their growth and for the repair of waste, but by means of which they are able to get rid of the worn-out matters which need immediate removal. In vertebrate animals the blood has a red colour and a temperature above the medium in which the animal lives; in mammalia, and especially in birds, this artificial warmth is plainly noticed. The temperature of the blood is singularly constant in different animals under the most varying conditions of climate; it is 36°·9 (98° F.) in man, and 42°·8 (or 109° F.) in birds. The chief peculiarity of blood is the existence in it of very small round or oblong discs, differing in size and shape in different animals (diameter 0·0075 mm. in man, and four times as large in frogs). These are called the blood corpuscles; they float in a colourless liquid; a few of them are white, but the larger proportion are of a red colour; when the fibrin coagulates, it mechanically carries down these globules with it.

Healthy human blood possesses the following average composition, and its *specific gravity* is 1·055:

Coagulum, or Clot.	Fibrin	0·30	13·0
	Corpuscles	12·70	
Serum.	Water	79·00	87·0
	Albumin	7·00	
	Fatty matters	0·06	
	Salts	0·94	

The colour of the blood corpuscles is due to a substance called *Hæmoglobin*, which can be separated from the blood of most animals in the form of red microscopic crystals. This substance is an example of a body more complicated than albumin, which indeed it yields as a product of decomposition when subjected to the action of acids. Hæmoglobin contains the constant amount of 0·42 per cent. of iron. When treated with even very dilute acids it splits up into albumin and a body called *Hæmatin*, which was formerly considered to be the true colouring matter of blood. Hæmatin contains about 7 per cent. of iron.

Hæmoglobin forms a loose but yet true chemical combination with oxygen, and it is in virtue of the hæmoglobin which they contain that the blood corpuscles serve as the oxygen-carriers of the body.

In all warm-blooded animals two kinds of blood exist; red, or arterial blood, contained in the left side of the heart and in the arteries, and purple, or venous blood, contained in the right side of the heart and in the veins. *Venous* blood is blood which having circulated through the body has parted with a considerable proportion of the loosely-combined oxygen of its hæmoglobin, and which is charged with certain products of the waste of the tissues. *Arterial* blood is such as having circulated through the lung has thus got rid of a considerable proportion of the carbonic acid gas which it had acquired in its circulation through the system, and which has absorbed rather more than an equal volume of oxygen gas, which, combining with the hæmoglobin, is carried by it throughout the body to be given up by it to oxidizable substances.

Oxygen, carbonic acid, and nitrogen are contained in blood, partly in a state of loose chemical combination, partly in a state of solution. As a rule the first of them is present only in the former of these states; the second exists partly in a state of solution and partly in a state of chemical combination; the third appears to be simply dissolved. Whilst the oxygen is almost entirely present in the corpuscles, the carbonic acid and hydrogen are constituents of the *liquor sanguinis*. The carbonic acid of the blood, which is not simply dissolved, appears to be retained in great part by the neutral sodium phosphate (Na_2HPO_4). which the *liquor sanguinis* contains. By boiling the blood in a Torricellian vacuum, not only are the gases evolved which are held in a state of simple solution, but also those which exist in loose chemical combination, in the corpuscles or in the *liquor sanguinis*, a dissociation of the compounds occurring under these circumstances.

The following table exhibits the quantity and composition of the gases (measured at 0° and under the pressure of 1 meter of mercury), yielded on an average by 100 volumes of arterial and venous blood:

	100 volumes of arterial blood yield	100 volumes of venous blood yield
O	16·9	6·0
CO_2	30·0	35·0
N	1 to 2	1 to 2

The brain contains many imperfectly investigated substances, amongst which is to be mentioned one, rich in phosphorus, called *Protagon*, which appears to be a glucoside of a complicated body called *Lecithin* (see p. 378). The products of decomposition of the latter body are stearic acid, glycerolphosphoric acid, and an ammonium base called *Neurine*.

Amongst the other most important animal fluids may be mentioned *Gastric Juice*, a clear liquid secreted by the lining membrane of the stomach; this secretion contains a substance called *Pepsin*, which is the active agent in effecting the digestion and solution of the albuminous parts of the food. It has an acid reaction due to the presence of free lactic and hydrochloric acids. The *Bile*, a liquid secreted in the liver and poured out into the duodenum: this substance contains several peculiar nitrogenized acids, viz. *taurocholic acid*, $C_{26}H_{45}NSO_7$, and *glycocholic acid*, $C_{26}H_{43}NO_6$. A peculiar substance termed *Taurin*, $C_2H_7NSO_3$, is obtained by the action of acids on bile: this body, which is isomeric with the compound of aldehyde-ammonia and sulphur dioxide, can be prepared artificially by heating ammonium isethionate, $H_4NC_2H_5SO_4$, which parts with H_2O, and forms taurin.

Milk.—The composition of this important secretion varies considerably in different animals, but each kind contains all the materials needed for the formation of the body of the young animal; thus it contains casein (a body having nearly the same composition as flesh), fats (butter), and milk-sugar, together with those inorganic salts, especially the alkaline chlorides and calcium phosphates, needed for the formation of bone. The following gives the average composition of milk of different animals:

	Woman.	Cow.	Goat.	Ass.	Bitch.
Water	88·6	87·4	82·0	90·5	66·3
Butter	2·6	4·0	4·5	1·4	14·8
Milk-Sugar and Soluble Salts	4·0	5·0	4·5	6·4	2·9
Casein and Insoluble Salts	3·9	3·6	9·0	1·7	16·0

The specific gravity of milk varies from 1·03 to 1·04.

The Urine.—It is in the urine that a large portion of the waste nitrogenous portions of the body pass off as urea and uric acid. The urine is secreted by the kidneys from the arterial blood. Healthy urine contains, in 1,000 parts, 957 parts of water, 14 of urea, 1 of uric acid, 15 of other organic matter, and 13 of inorganic salts.

FUNCTIONS OF ANIMALS AND PLANTS

The general characteristics of *animal* and *vegetable* life may be stated as follows: the animal lives upon *organized* materials, taking up oxygen and evolving carbonic acid and other oxidized products; the plant lives upon *unorganized* materials, especially carbonic acid, water, ammonia, and salts, organizing them and evolving oxygen. The chemical function of the animal is oxidation, that of the plant reduction. The food of the plant serves merely to increase its bulk: that of the animal is employed (after it has attained its full growth) to replace the material worn out by all the active operations of life. The animal obtains the energy necessary for its existence from the oxidation of its own body; the plant obtains the energy necessary for the organization of its food directly from the sun.

Respiration and Animal Heat.—The process of respiration, essential to the life of all animals, consists in the aërating of the blood, circulating through the lungs or similar apparatus, by means of the oxygen of the air. The blood does not come into actual contact with the air, but is separated by a large surface of very thin membrane, through which the exchange of gases takes place by solution and diffusion. Not only does the blood gain in oxygen (see Blood, p. 446), but it loses the products of combustion with which it is charged, and is thus rendered fit again to circulate and carry away used-up material. The volume of air thrown out of the human lungs at each ordinary expiration amounts to from 350 to 700 cubic centimeters: this, however, by no means empties the lungs, whose capacity is much greater: the number of respirations amounts to about fifteen in each minute. The expired air differs remarkably from the inspired air, as it contains from 3 to 6 per cent. of carbonic acid, and will not support the combustion of a candle.

Under different circumstances of health or disease, activity or repose, sleeping or waking, after a meal or fasting, according to the temperature, pressure of the air, and other varying causes, the quantity of exhaled carbonic acid varies considerably. The determination of the quantity of carbonic acid exhaled by an animal under the above circumstances is a subject of the highest importance, but one which is surrounded by numerous experimental difficulties.

We may assume, as the result of the best experiments, that a man gives off 19·8 liters of carbonic acid (at 0° and 760 mm.) each hour; this amounts to about 40 grams of carbonic acid, or 10·6 grams of carbon, per hour: the heat which is always evolved by the combustion of this carbon goes to keep up the temperature of the body. It is difficult to determine with accuracy how far the whole of the animal heat can be accounted for by the combustion of this carbon, as the chemical changes which go on in the body are of a very complicated nature, and as yet little understood. Considering, however, the subject in a general point of view, there cannot be much doubt that the whole of the animal heat is derived from the combustion of the materials of the body: thus we find that in birds, whose temperature is higher than that of mammalia, the quantity of carbonic acid evolved is more than half as much again as in larger animals; whilst in cold climates, where the loss of animal heat is great, men find it necessary to eat enormous quantities of fat, this doubtless serving to maintain the temperature of the body.

The effect of starvation on the quantities of carbonic acid and urea excreted, taken as representing the rate of change going on in the body, is very remarkable: in a dog, the quantity of carbonic acid was reduced by fasting for ten days to one-third, and the urea to one twenty-second part of the amount given off on full diet; whereas in a man the carbonic acid was nearly reduced to one-third by starvation. An interesting fact has been observed, viz., that hydrogen and marsh gas are evolved in small quantities from the skin and lungs under certain conditions.

This subject is quite in its infancy, and demands careful experimental investigation, as it is by such patient research alone that we can hope to form any real estimate of the income and expenditure of the body. The special study of the chemistry of the body has been made a separate branch of science, termed *Physiological Chemistry.*

FOOD OF PLANTS

Animals, as we have seen, are unable to produce the complicated chemical compounds which they need for their structure; plants are, however, able to do this, and from the elementary constituents to build up their various parts. This function of plants is entirely dependent upon the sunlight; without sunlight the green colouring matter of the leaves of plants cannot decompose the atmospheric carbonic acid, and therefore, without sunlight the plant cannot grow.

In order to separate the atoms of carbon and oxygen, an expenditure of force is necessary; this force is derived from the rapidly vibrating solar rays: it is they which tear asunder the carbon and oxygen atoms, and thus enable the leaves to take up and assimilate the carbon, throwing out the oxygen into the air for the subsequent use of animals. When vegetable matter is ignited, it burns to carbonic acid, and generates exactly the same amount of energy as was originally needed in the form of vibrations of light to decompose the atmospheric carbonic acid. Hence, when coal burns, the light and heat evolved may truly be said to be that of the sun; and, as animals depend for their existence upon vegetables, and these in their turn cannot live without the solar radiations, animals may with truth be called children of the sun.

The bodies of plants may be considered to be composed of two kinds of substances: *organic*, such as starch, vegetable fibre, &c.; and *inorganic* salts, constituting the ash of the plant. The plant obtains the carbon needed for the first of these materials, mainly from the atmosphere; the nitrogen, hydrogen, and oxygen, which the organic substances contain, the plant takes up both by its leaves and by its roots; whilst the whole of the inorganic salts are absorbed from the earth by the roots, which act as the mouth of the plant, whilst the leaves may be compared to the lungs of animals. Every plant has in the atmosphere an unlimited supply of carbon and water; but for the supply of inorganic materials the plant is dependent upon the nature of the particular soil in which it grows, and hence the value of artificially supplying these constituents when the soil becomes impoverished. Plants possess the peculiar power of selection, by the roots, of the mineral constituents of food, as well as the subsequent chemical elaboration of the materials. Of the causes of the changes which thus go on we know nothing: thus, we cannot explain why an acorn turns out always to be an oak, or why of two seeds sown in the same soil, and exposed to the same sunlight and air, one evolves a poisonous and the other a wholesome plant.

Concerning the growth of plants a large amount of information has been amassed, but we are far from possessing even an approach to a knowledge of the laws of this important subject. For an account of the interesting facts which have been ascertained respecting the questions of manuring, fertility of the soil, &c., we must refer the reader to books on the branch science of *Agricultural Chemistry.*

LESSON XLIII

SYNTHETICAL PRODUCTION OF ORGANIC COMPOUNDS

THE chief constituents of animal and vegetable bodies consist of carbon compounds; most of them contain in addition to this element hydrogen and oxygen, and often also nitrogen. These are all formed from carbonic acid, water, and nitrogen or ammonia, but the manner in which this combination takes place is at present quite unknown to us. For a long time it was believed that compounds occurring in vegetable or animal bodies could not be prepared artifically, "vital force" being necessary for their production. In the year 1828, however, Wöhler showed that ammonium cyanate, a substance obtained from inorganic sources, is converted on heating into urea, which had hitherto only been obtained from animal organisms (p. 308). From that time the belief in the so-called "vital force" gradually disappeared, as numbers of other animal and vegetable products were soon prepared artificially. Not only so, but a large number of other allied compounds which do not occur in nature, were obtained by synthesis, and now, as has already been stated, the number of carbon compounds known far exceeds that of all the others put together.

Many of the synthetical productions of carbon compounds have been mentioned in the previous pages; the synthesis of the more important naturally occurring compounds, as well as the general synthesis of certain classes of organic compounds, and known as the *aceto-acetic* and *malonic* synthesis, may be shortly summarized here.

One of the simplest naturally occurring organic compounds is *formic acid*, (p. 335) which occurs in ants and stinging nettles. It may be artificially prepared by bringing moist carbon dioxide and potassium together:

$$2CO_2 + H_2O + K_2 = KHCO_3 + KCHO_2,$$

or by heating carbonic oxide with strong caustic potash:

$$CO + KOH = KCHO_2.$$

From the potassium salt the free acid may be obtained by the action of dilute mineral acids.

When carbon dioxide is passed over heated potassium it yields the potassium salt of oxalic acid, a compound widely distributed in the animal and vegetable kingdom (p. 365).

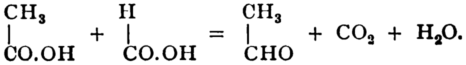
$$2CO_2 + K_2 = K_2C_2O_4.$$

When a mixture of carbon disulphide and sulphuretted hydrogen is passed over red hot copper, methane or marsh-gas is formed:

$$CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S.$$

This compound, as already mentioned, is the simplest organic compound; by suitable reactions we can however convert it into more complicated substances. Thus by the action of chlorine, an atom of hydrogen is replaced by the latter element forming the compound CH_3Cl, which on heating with zinc yields ethane, C_2H_6, or $CH_3.CH_3$, in which two carbon atoms are united together. If we replace another atom of hydrogen in ethane by methyl or ethyl, we get propane, C_3H_8 or butane C_4H_{10}, and are thus enabled to prepare the series of paraffin hydrocarbons and obtain from them their numerous derivatives, many of which, *e.g.* the fatty acids, occur in nature.

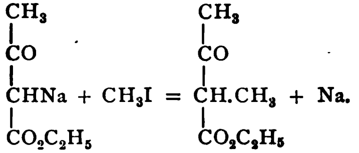
When the above mentioned methyl chloride is treated with potassium cyanide it yields methyl cyanide or acetonitrile CH_3CN, which on boiling with acids or alkalis yields acetic acid, $CH_3.COOH$. If the calcium salt of acetic acid be heated with calcium formate it yields aldehyde:



$$\begin{array}{l} CH_3 \\ | \\ CO.OH \end{array} + \begin{array}{l} H \\ | \\ CO.OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CHO \end{array} + CO_2 + H_2O.$$

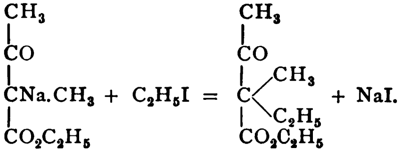
The latter on reduction yields common alcohol, $C_2H_5.OH$, which in turn may be converted into ethyl cyanide or propionitrile, C_2H_5CN, and propionic acid, $C_2H_5.COOH$, and so on up the series of alcohols and fatty acids.

A much more important synthesis of the fatty acids is that known as the *aceto-acetic synthesis.* By the action of sodium on ethyl acetate it is converted into *ethyl sodaceto-acetate,* $CH_3.CO.CHNa.CO_2C_2H_5$, which, when treated with dilute acids yields *ethyl aceto-acetate* or *aceto-acetic ether,* $CH_3.CO.CH_2.CO_2C_2H_5$. If the former be treated with an alcoholic iodide or bromide the following reaction takes place :



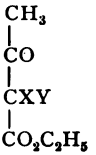
$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHNa \\ | \\ CO_2C_2H_5 \end{array} + CH_3I = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH.CH_3 \\ | \\ CO_2C_2H_5 \end{array} + Na.$$

By the further action of sodium on this compound the second hydrogen atom in the methylene group may be replaced by sodium, and the latter again by a methyl or other alcohol radical, *e.g.* ethyl.



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CNa.CH_3 \\ | \\ CO_2C_2H_5 \end{array} + C_2H_5I = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C\begin{array}{l} \diagup CH_3 \\ \diagdown C_2H_5 \end{array} \\ | \\ CO_2C_2H_5 \end{array} + NaI.$$

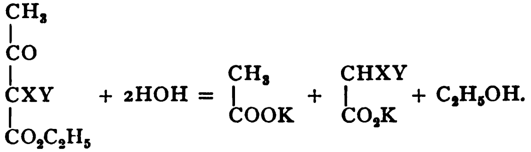
It will thus be seen that in ethyl aceto-acetate we can replace one or both of the hydrogen atoms by the same or different alcohol radicals, the compounds formed have the general formula :



$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CXY \\ | \\ CO_2C_2H_5 \end{array}$$

when X and Y are either hydrogen or an alcohol radical.

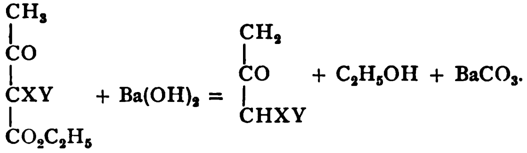
If these compounds be heated with strong alcoholic potash the following reaction takes place :



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CXY} \\ | \\ \mathrm{CO_2C_2H_5} \end{array} + \mathrm{2HOH} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{COOK} \end{array} + \begin{array}{l} \mathrm{CHXY} \\ | \\ \mathrm{CO_2K} \end{array} + \mathrm{C_2H_5OH}.$$

By introducing different alcohol radicals into ethyl aceto-acetate and acting on the product with alcoholic potash we can therefore obtain a large number of fatty acids of different constitution.

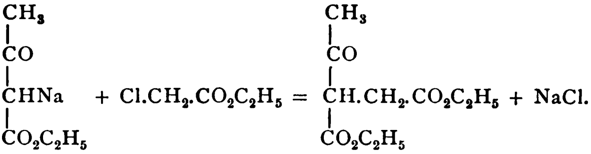
If the above compound $\mathrm{CH_3.CO.CXY.CO_2C_2H_5}$ be heated with a milder alkali such as baryta, a different reaction takes place :



$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CXY} \\ | \\ \mathrm{CO_2C_2H_5} \end{array} + \mathrm{Ba(OH)_2} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CHXY} \end{array} + \mathrm{C_2H_5OH} + \mathrm{BaCO_3}.$$

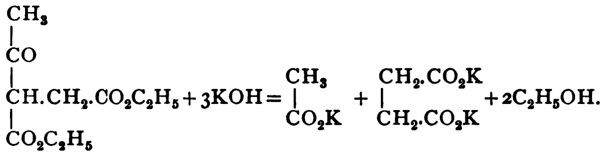
This, therefore, also forms a ready method of obtaining ketones by synthesis.

The aceto-acetic synthesis may also be varied in other ways, of which the following is an example : when ethyl sodaceto-acetate is treated with ethyl chloracetate, the following reaction takes place :



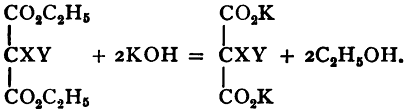
$$\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CHNa} \\ | \\ \mathrm{CO_2C_2H_5} \end{array} + \mathrm{Cl.CH_2.CO_2C_2H_5} = \begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{CH.CH_2.CO_2C_2H_5} \\ | \\ \mathrm{CO_2C_2H_5} \end{array} + \mathrm{NaCl}.$$

The compound formed is decomposed by caustic potash as follows, forming acetic acid, alcohol, and succinic acid (p. 367).



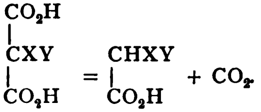
$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH.CH_2.CO_2C_2H_5\\ |\\ CO_2C_2H_5\end{array} + 3KOH = \begin{array}{l}CH_3\\ |\\ CO_2K\end{array} + \begin{array}{l}CH_2.CO_2K\\ |\\ CH_2.CO_2K\end{array} + 2C_2H_5OH.$$

Another important method of obtaining fatty acids is the *malonic synthesis*, which is very similar to the foregoing. It is carried out by replacing one or both of the hydrogen atoms in the methylene group of ethyl malonate, $CO_2C_2H_5.CH_2.CO_2C_2H_5$, by alcoholic radicals, and boiling the compound formed with alcoholic potash:



$$\begin{array}{l}CO_2C_2H_5\\ |\\ CXY\\ |\\ CO_2C_2H_5\end{array} + 2KOH = \begin{array}{l}CO_2K\\ |\\ CXY\\ |\\ CO_2K\end{array} + 2C_2H_5OH.$$

The free dicarboxylic acid is obtained by the action of acids, and on distillation loses carbon dioxide forming the corresponding fatty acid:

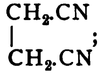


$$\begin{array}{l}CO_2H\\ |\\ CXY\\ |\\ CO_2H\end{array} = \begin{array}{l}CHXY\\ |\\ CO_2H\end{array} + CO_2.$$

Acetic acid may also be converted by a series of reactions into glycerol; thus calcium acetate on heating yields acetone $(CH_3)_2CO$, which on reduction yields isopropyl alcohol $(CH_3)_2CH.OH$; from the latter isopropyl iodide $(CH_3)_2CHI$ may be prepared, which is converted by chloride of iodine into propenyl chloride, $CH_2Cl.CHCl.CH_2Cl$. This compound on heating with water under pressure yields *glycerol*. $CH_2(OH).CH(OH).CH_2.OH$, and glycerol on further heating with fatty acids yields the *naturally occurring fats*.

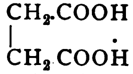
When glycerol is suitably oxidized it first yields glyceric aldehyde, which then polymerizes forming members of the sugar group, the chief produce being *acrose* or *inactive fructose* (p. 386).

If a strong electric current be passed between carbon poles in an atmosphere of hydrogen, the carbon and hydrogen combine to form *acetylene*, C_2H_2, which is converted by nascent hydrogen into *ethylene*, C_2H_4. This combines directly with bromine forming ethylene bromide, $C_2H_4Br_2$, the bromine atoms in which may be readily replaced by CN forming ethylene cyanide,



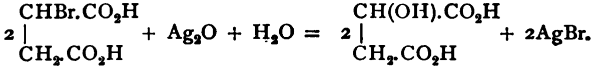
$\begin{array}{l}CH_2.CN\\|\\CH_2.CN\end{array}$

; the latter is converted by acids into succinic acid,

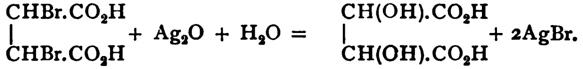


$\begin{array}{l}CH_2.COOH\\|\\CH_2.COOH\end{array}$

. Bromine acts on succinic acid forming a mono- and a dibromo-derivative, which are converted by moist silver oxide into *malic* and *tartaric acid* respectively

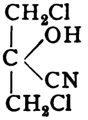


$$2\begin{array}{l}CHBr.CO_2H\\|\\CH_2.CO_2H\end{array} + Ag_2O + H_2O = 2\begin{array}{l}CH(OH).CO_2H\\|\\CH_2.CO_2H\end{array} + 2AgBr.$$

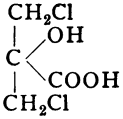


$$\begin{array}{l}CHBr.CO_2H\\|\\CHBr.CO_2H\end{array} + Ag_2O + H_2O = \begin{array}{l}CH(OH).CO_2H\\|\\CH(OH).CO_2H\end{array} + 2AgBr.$$

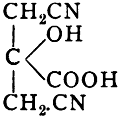
When glycerol is treated with hydrochloric acid, it yields dichlorhydrin, $CH_2Cl.CH(OH).CH_2Cl$, which, on oxidation, yields dichloracetone, $CH_2Cl.CO.CH_2Cl$; this combines with HCN forming the compound



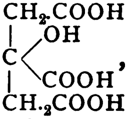
which yields the corresponding acid



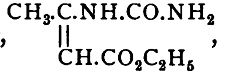
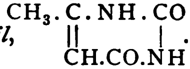
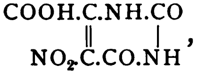
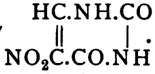
on treatment with acids. By the action of the potassium cyanide the two chlorine atoms may be replaced by cyanogen and the resulting compound

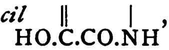
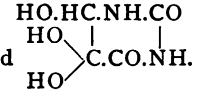


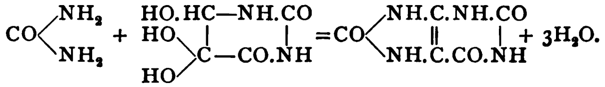
on treatment with acids yields



, which is the well-known natural product *citric acid.*

Another important synthesis of a naturally occurring product is that of *uric acid.* This is obtained in the following manner: urea combines with ethyl aceto-acetate forming *ethyl uramidocrotonate*,  $\begin{array}{l} CH_3.C.NH.CO.NH_2 \\ \| \\ CH.CO_2C_2H_5 \end{array}$, which readily loses alcohol, forming *methyluracil*,  $\begin{array}{ll} CH_3.C.NH & .CO \\ \| & | \\ CH.CO & .NH \end{array}$. Nitric acid converts the latter into *nitrouracilcarboxylic acid*,  $\begin{array}{ll} COOH.C.NH & .CO \\ \| & | \\ NO_2.C.CO & .NH \end{array}$, which readily loses CO_2 passing into *nitrouracil*  $\begin{array}{ll} HC.NH & .CO \\ \| & | \\ NO_2C.CO & .NH \end{array}$.

On reduction the latter yields a mixture of amido-uracil and *oxyuracil*  $\begin{array}{ll} HC.NH & .CO \\ \| & | \\ HO.C.CO & .NH \end{array}$, which on oxidation with bromine water yields the compound  $\begin{array}{ll} HO.HC.NH & .CO \\ HO\diagdown \quad | & | \\ \quad \rangle C.CO & .NH \\ HO\diagup & \end{array}$. If this be heated with urea and sulphuric acid on the water bath, the following reaction takes place:



$$CO\begin{array}{l}\diagup NH_2 \\ \diagdown NH_2\end{array} + \begin{array}{ll} HO.HC—NH & .CO \\ HO\diagdown \quad | & | \\ \quad \rangle C—CO & .NH \\ HO\diagup & \end{array} = CO\begin{array}{ll}\diagup NH.C.NH & .CO \\ \quad \| & | \\ \diagdown NH.C.CO & .NH\end{array} + 3H_2O.$$

uric acid being formed.

If acetylene is passed through a tube heated almost to redness it is converted into benzene.

$$3C_2H_2 = C_6H_6.$$

As all aromatic substances contain the benzene nucleus and may be derived from this hydrocarbon by replacing its hydrogen by other elements or radicals, we can also prepare these compounds synthetically in the laboratory. Thus benzene by the action of bromine yields *bromobenzene*, C_6H_5Br, which on heating with methyl iodide and sodium yields toluene.

$$C_6H_5Br + CH_3I + 2Na = C_6H_5.CH_3 + NaBr + NaI.$$

Many other hydrocarbons may be prepared in a similar manner. If bromobenzene be treated with sodium and carbon dioxide it yields benzoic acid, which was originally obtained from gum benzoin :

$$C_6H_5Br + Na_2 + CO_2 = C_6H_5.CO_2Na + NaBr.$$

If the amide of this acid be heated with chloracetic acid we get *hippuric acid*, which is contained in the urine of graminivorous animals :

$$C_6H_5.CO.NH_2 + CH_2Cl.CO_2H = C_6H_5.CO.NH.CH_2.CO_2H + HCl.$$

Benzene may be readily converted into phenol (p. 400), and the sodium compound of the latter when treated with carbon dioxide yields the sodium salt of salicylic acid.

$$CO_2 + 2C_6H_5ONa = C_6H_4(ONa)CO_2Na + C_6H_5OH.$$

This acid occurs in the flowers of *Spiraea ulmaria*, and its methyl ether is the winter green oil obtained from *Gaultheria procumbens*. Salicylic acid may be converted into di-iodosalicylic acid, and this on fusion with potash yields the gallic acid found in gall-nuts

$$C_6H_2I_2(OH).CO_2H + 3KOH = C_6H_2(OH)_3.CO_2K + 2KI + H_2O.$$

Cinnamic acid, which occurs in Styrax, Peru balsam, &c., may be readily obtained artificially by heating benzaldehyde with sodium acetate and a dehydrating agent such as acetic anhydride :

$$C_6H_5.CHO + CH_3.CO_2Na = C_6H_5.CH{=}CH.CO_2Na + H_2O.$$

In addition to these the syntheses of the important colouring matters, indigo and alizarin have already been described (pp. 423, 427), as has also that of the alkaloid coniine (p. 436). That of the other more important alkaloids such as quinine, morphine, &c., is only a question of time. It may indeed be now said that any organic compound, so long as it does not possess an organized structure, may be synthesized as soon as its constitution is accurately known.

By Act of Parliament (27 *and* 28 *Vict. cap.* 117, 29*th July*, 1864), *the use of the Metrical System of Weights and Measures is rendered legal. The Weight of the Kilogram is settled by this Act to be equal to* 15432·3487 *English grains.*

COMPARISON OF THE METRICAL WITH THE COMMON MEASURES. By Dr. Warren de la Rue.

MEASURES OF LENGTH.

	In English Inches.	In English Feet = 12 Inches.	In English Yards = 3 Feet.	In English Fathoms = 6 Feet.	In English Miles =1,760 Yards.
Millimeter	0·03937	0·0032809	0·0010936	0·0005468	0·0000006
Centimeter	0·39371	0·0328090	0·0109363	0·0054682	0·0000062
Decimeter	3·93708	0·3280899	0·1093633	0·0546816	0·0000621
Meter	39·37079	3·2808992	1·0936331	0·5468165	0·0006214
Decameter	393·70790	32·8089920	10·9363310	5·4681655	0·0062138
Hectometer	3937·07900	328·0899200	109·3633100	54·6816550	0·0621382
Kilometer	39370·79000	3280·8992000	1093·6331000	546·8165500	0·6213824
Myriometer	393707·90000	32808·9920000	10936·3310000	5468·1655000	6·2138244

1 Inch = 2·539944 Centimeters.
1 Foot = 3·0479449 Decimeters.

1 Yard = 0·91438348 Meters.
1 Mile = 1·6093140 Kilometers.

MEASURES OF SURFACE.

	In English Square Feet.	In English Sq. Yards = 9 square Feet.	In English Poles = 272·25 Sq. Feet.	In English Roods=10,890 Sq. Feet.	In English Acres=43,560 Sq. Feet.
Centiare or square meter	10·7642993	1·1960333	0 0395383	0·000988457	0·0002471143
Are or 100 square meters	1076·4299342	119·6033260	3·9538290	0·098845724	0·0247114310
Hectare or 10,000 square meters .	107642·9934183	11960·3326020	395·3828959	9·884572398	2·4711430996

1 Square Inch = 6·4515669 Square Centimeters.
1 Square Foot = 9·2899683 Square Centimeters.

1 Square Yard = 0·83609715 Square Meter or Centiare.
1 Acre = 0·404671021 Hectare.

MEASURES OF CAPACITY.

	In Cubic Inches.	In Cubic Feet = 1,728 Cubic Inches.	In Pints = 34·65923 Cubic Inches.	In Gallons = 8 Pints. = 277·27384 Cubic Inches.	In Bushels = 8 Gallons = 2218·19075 Cubic Inches.
Milliliter or cubic centimeter . . .	0·061027	0·0000353	0·001761	0·00022010	0·000027512
Centiliter or 10 cubic centimeters.	0·610271	0·0003532	0·017608	0·00220097	0·000275121
Deciliter or 100 cubic centimeters.	6·102705	0·0035317	0 176077	0·02200967	0 002751208
Liter or cubic decimeter	61·027052	0·0353166	1·760773	0·22009668	0·027512085
Decaliter or centistere	610·270515	0·3531658	17·607734	2·20096677	0·275120846
Hectoliter or decistere	6102·705152	3·5316581	176·077341	22·00966767	2·751208459
Kiloliter or stere, or cubic meter .	61027·051519	35·3165807	1760·773414	220·09667675	27·512084594
Myrioliter or decastere	610270·515194	353·1658074	17607·734140	2200·96676750	275·120845937

1 Cubic Inch = 16·3861759 Cubic Centimeters. 1 Cubic Foot = 28·3153119 Cubic Decimeters.
1 Gallon = 4·543457969 Liters.

MEASURES OF WEIGHT.

	In English Grains.	In Troy Ounces = 480 Grains.	In Avoirdupois Lbs. = 7,000 Grains.	In Cwts. = 112 Lbs. = 734,000 Grains.	In Tons. = 20 Cwt. = 15,620,000 Grains.
Milligram	0·015432	0·000032	0·0000022	0·00000002	0·000000001
Centigram	0·154323	0·000322	0·0000220	0·00000020	0·000000010
Decigram	1·543235	0·003215	0·0002205	0·00000197	0·000000098
Gram	15·432349	0·032151	0·0022046	0·00001968	0·000000984
Decagram	154·323488	0·321507	0·0220462	0·00019684	0·000009842
Hectogram	1543·234880	3·215073	0·2204621	0·00196841	0·000098421
Kilogram	15432·348800	32·150727	2·2046213	0·01968412	0·000984206
Myriogram	154323·488000	321·507267	22·0462126	0·19684118	0·009842059

1 Grain = 0·06479895 Gram.
1 Troy oz. = 31·103496 Grams.

1 Lb. Avd. = 0·45359265 Kilogr.
1 Cwt. = 50·80237689 Kilogr.

QUESTIONS AND EXERCISES UPON THE FOREGOING LESSONS.

IN order to enable the pupil to master the principles of the science, he must conscientiously write out answers to the Questions, and work out the Exercises given in illustration of each Lesson. In actual teaching it will be found necessary to supplement the Questions given below by many others of a like character.

LESSON I. *Introduction.*

1. Define the objects of the science of chemistry. With what other sciences does it stand in near relation?

2. When a candle burns there is apparently a loss of material. Is this really the case? Explain your conclusion fully.

3. Do you consider that this one experiment entitles one to state as a general law that matter is indestructible? What other experiments support the law?

4. What means would you propose to employ for the sake of determining whether a given body were elementary or compound?

5. What are the essential requisites in a chemical balance?

6. Name ten of the commonest elements. Is it likely that we are acquainted with all the elements existing on the earth?

LESSON II. *Oxygen and Hydrogen.*

1. How did Priestley first prepare oxygen, and why was this name given to it by Lavoisier?

2. Describe in detail the process generally adopted for obtaining and collecting the gas.

3. I want ten grams of oxygen; how many grams of $KClO_3$ must I take?

4. What is meant by the combining weights of the elements? Give examples.

5. How can ozone be obtained? How does it differ from ordinary oxygen?

6. How can hydrogen be obtained from water? What happens when hydrogen is burnt in air?

7. 64·9 parts by weight of zinc in decomposing sulphuric acid set free 2 parts by weight of hydrogen. How much zinc must be employed to obtain 10 grams of hydrogen?

8. How would you show in a striking manner the extreme lightness of hydrogen? A liter of hydrogen weighs 0·0896 grams; how much does a liter of oxygen weigh?

LESSON III. *Physical Properties of Gases, &c.*

[It will generally be found necessary to divide this into several lessons, and to familiarise the pupil with the subject by a much larger number of exercises than those here given.]

1. A gram is the weight of a cubic centimeter of water at 4° Centigrade, a meter is 39·37 English inches; what is the volume occupied by a kilogram of water and the number of millimeters in an English inch?

2. How is a Centigrade thermometer graduated?

How many degrees C. and R. correspond to + 43° and — 22° F.?
" C. and F. " + 327° and — 2° R.?
" F. and R. " + 78° and — 172° C.?

3. What alterations in volume do gases undergo when exposed (*a*) to heat, (*b*) to pressure?

4. A vessel surrounded by melting ice contains 273 cc. of a perfect gas; what volume will this gas occupy if free to expand when the vessel is surrounded by steam at 100° C.?

5. When the barometer stands at 735 mm. the volume of gas in a certain vessel is exactly a liter, what is the volume when the barometer is at 770 mm. assuming the temperature to have remained constant?

6. What volume will 1,000 cc. of oxygen at 0° and 760 mm. become at a temperature of 16·5°, and under a pressure of 735 mm.?

7. Two grams of hydrogen occupy at 0° and 760 mm. pressure 22·4 liters. How many grams will 22·4 liters of oxygen weigh under the same conditions?

8. Find the volume of oxygen yielded by heating 13·5 grams of HgO ($Hg = 200$, $O = 16$).

9. What is the weight in grams of 516 liters of hydrogen gas measued at 20° — and under 770 mm. pressure?

10. What is the weight of 10 liters of oxygen, of chlorine, and of nitrogen at 0° C. and 760 mm. pressure?

11. A bottle containing hydrogen and one containing CO_2 and closed with stucco, are left standing in the air; what will happen?

12. What means are used to liquefy gases? What gases are the most difficult to liquefy?

LESSON IV. *Water and Peroxide of Hydrogen.*

1. How did Cavendish determine the composition of water?
2. Describe the most exact methods of determining the composition of water (1) by volume, (2) by weight.
3. What is meant by the latent heat of water? How is this determined? How is the latent heat of steam determined?
4. How can you show that when a liquid solidifies heat is given out?
5. Describe the changes in bulk which water undergoes when heated from 0° to 100°.
6. When does water boil?
7. Explain with a drawing Carré's apparatus for freezing water by its own evaporation.
8. Define the term "thermal unit."
9. How is the tension of aqueous vapour measured?
10. Why must the barometric pressure be noticed when graduating a thermometer?
11. What is the weight in grams of 22·4 liters of steam at 100° and 760 mm. of mercury?
12. How is H_2O_2 prepared, and what are its properties?

LESSON V. *Nitrogen and the Atmosphere.*

1. How would you deprive the air in a vessel of its oxygen? What change in properties would be observed in air so treated?
2. What reason have we for believing that the air is a mechanical mixture, and not a chemical combination of nitrogen and oxygen?
3. Describe the mode of making a eudiometric analysis of the air.
4. How may we determine the composition of the air by weight as regards nitrogen and oxygen?
5. Draw and describe an apparatus for estimating the quantity of carbonic acid gas contained in the air.

6. How is the composition of air affected by (*a*) animal life, (*b*) vegetable life, (*c*) combustion?

7. Is the quantity of moisture required to saturate a given volume of air always the same?

8. How would you estimate the weight of moisture in a given volume of air?

9. Name other constituents of the atmosphere.

10. The density of air is 14·435 times that of hydrogen; what weight of air at 0° C. and 760 mm. is contained in a room 5 meters long, 4 wide, and 3 high?

LESSON VI. *Nitric Acid and Oxides of Nitrogen.*

1. Give the composition by weight of the five oxides of nitrogen.

2. Explain what is meant by chemical combination in multiple proportions.

3. State the principles of Dalton's atomic theory.

4. What relation exists between the densities of elements in the gaseous state and their atomic weights?

5. State the law respecting the density of compound gases; give the densities of steam, ammonia, and carbon dioxide.

6. Calculate the weight of one liter of hydrochloric acid gas at 0° and 760 mm.

7. What happens when electric sparks are passed through the air?

8. Write out in symbols the decomposition occurring in the preparation of nitric acid, and explain the meaning of these symbols.

9. I want 500 grams of pure nitric acid; how many grams of nitre and sulphuric acid shall I need, and how many grams of hydrogen potassium sulphate will remain?

10. Mention the tests for nitric acid.

11. How is nitrogen pentoxide prepared?

12. 100 parts by weight of this substance contain 25·99 parts of nitrogen, and 74·01 parts of oxygen. Show that the formula of the substance is N_2O_5.

LESSON VII. *Oxides of Nitrogen and Ammonia.*

1. Name the chief properties of laughing gas.

2. How many grams of nitrogen monoxide and water can be obtained from 213 grams of ammonium nitrate?

3. How is the composition by volume of nitrous oxide gas determined?

4. I want 100 liters of nitric oxide gas when the temperature is 0° and the pressure 760 mm.; what weight in grams of copper and nitric acid must I take?

5. Point out the relation between nitrogen pentoxide and the nitrates, and nitrogen trioxide and the nitrites.

6. Give the formulæ representing two different modes by which ammonia can be produced.

7. How many liters of ammonia measured at 10° and under a pressure of 755 mm. can be obtained from 100 grams of sal-ammoniac?

8. Describe the principles of Carré's ammonia freezing machine.

9. How is the composition by volume of ammonia ascertained?

10. How can ammonia be liquefied?

11. How can pure nitrogen be obtained from ammonia?

12. Devise an experiment for showing the high degree of solubility of ammonia in water.

13. Give the composition of the compounds of nitrogen and hydrogen other than ammonia.

LESSON VIII. *Carbon and Carbon Dioxide.*

1. Name the three allotropic modifications of carbon. State their chief peculiarities.

2. Give some account of the occurrence of the different forms of carbon in the free state in nature, and also of carbon occurring in combination.

3. Give a short description of the nature of coal. What changes have occurred in the passage of wood into coal?

4. Required 572 grams of carbon dioxide; how will you obtain it, and what weight of materials will you need to use?

5. What law regulates the absorption of this gas in water?

6. How can carbon dioxide be obtained in the liquid and in the solid state? What peculiar property does this liquid exhibit?

7. Explain the mode adopted for obtaining very low temperatures by means of solid carbon dioxide.

8. Describe, with a drawing, the apparatus used to determine the composition of carbon dioxide.

9. State the results of this determination.

10. How many liters of carbon dioxide measured at 300°

and under a pressure of 740 mm. can be obtained by burning one kilogram of Wigan cannel (No. 5 on page 79)?

11. Describe an experiment showing that carbon dioxide contains its own volume of oxygen.

12. A specimen of coal is completely burnt in a stream of oxygen; how would you determine the weight of CO_2 and of H_2O formed, and calculate the C and H in the coal?

LESSON IX. *Carbon Monoxide and Hydrocarbons.*

1. How many grams of carbon will be needed to convert 100 liters of carbon dioxide at 0° and 760° into carbon monoxide, and how many liters of this latter gas will be formed?

2. Find the volume in liters at 10° and 740 mm. of carbon monoxide which can be obtained from 100 grams of oxalic acid and formic acid respectively.

3. How is the composition of carbon monoxide ascertained by eudiometric analysis?

4. What is the composition of marsh-gas and fire-damp?

5. How is olefiant gas prepared?

6. State shortly the properties and composition of coal gas.

7. Under what circumstances is acetylene formed and how can it be recognized?

8. Explain, with sketch, the structure of the flame of a candle. In what respects does it differ from that of a blowpipe or the Bunsen burner?

9. Explain the principles of the Davy lamp.

10. How many liters of carbon dioxide are formed by the complete combustion of one liter of olefiant gas?

11. How is cyanogen gas prepared?

12. I want 50 grams of pure hydrocyanic acid; how many grams of potassium cyanide and sulphuric acid shall I need to use?

LESSON X. *Chlorine.*

1. Write down as an equation the decompositions which occur in the preparation of chlorine from rock-salt.

2. I want 100 liters of chlorine gas at 10°, and under the pressure of 735 mm.; how many grams of the materials, viz., $NaCl$, H_2SO_4 and MnO_2 shall I require?

3. Describe experiments proving the power of chlorine to combine with hydrogen.

4. Explain the bleaching action of chlorine, and state what is meant by the nascent condition.

5. How many kilos. of salt and sulphuric acid must be taken to yield 100 kilos. of aqueous hydrochloric acid containing 20·22 per cent. of the gas?

6. How is the composition of hydrochloric acid determined?

7. Write out the formulæ of the oxides of chlorine and the corresponding acids.

8. Describe the action of water upon chlorine monoxide, nitrogen pentoxide, and carbon dioxide.

9. What is the composition of bleaching powder?

10. How is potassium chlorate prepared?

11. The percentage composition of potassium chlorate being potassium 31·92, chlorine 28·93, oxygen 39·15, show that its formula is $KClO_3$.

12. Show that the aqueous perchloric acid containing 72·3 per cent. of $HClO_4$ does not correspond to any definite compound of this acid with water.

LESSON XI. *Bromine, Iodine, and Fluorine.*

1. Describe the mode of obtaining pure bromine.

2. What is the composition of bromic and perbromic acids?

3. Write out in an equation the decompositions occurring in the manufacture of iodine from potassium iodide.

4. How is hydriodic acid gas prepared?

5. Show that the aqueous hydriodic acid, boiling at a constant temperature, and containing 57 per cent. of HI. does not correspond to a definite hydrate.

6. How would you detect iodine, bromine, and chlorine, when present in solution together?

7. How has fluorine been isolated?

8. Mention the most remarkable property of HF.

9. State the general relations which Cl, Br, I, and F exhibit amongst themselves.

10. What occurs when the following bodies are separately heated:—potassium iodate, barium iodate, iodine, and periodic acid?

11. How would you make some potassium bromate?

12. How would you distinguish between potassium bromate and potassium chlorate?

LESSON XII. *Sulphur and Sulphurous Acid.*

1. State the different compounds in which sulphur is met with in nature.

2. Sulphur occurs naturally, mixed with earthy impurities; how is it freed from these?

3. Name some of the chief properties of sulphur.

4. How can the prismatic and octohedral forms of sulphur respectively be obtained?

5. Write down the names and symbols of the compounds of sulphur, oxygen, and hydrogen.

6. How is sulphur dioxide prepared (*a*) from S, (*b*) from concentrated sulphuric acid?

7. How is real sulphurous acid formed from sulphur dioxide? Explain the constitution of the salts termed sulphites.

8. How does sulphurous acid act as a bleaching agent?

9. Find the percentage of sulphur in H_2SO_4, in zinc blende, and in iron pyrites.

10. How can sulphurous acid be converted into sulphuric acid?

LESSON XIII. *Sulphuric Acid and Sulphuretted Hydrogen.*

1. How is sulphur trioxide prepared, and what are its properties?

2. Describe the decompositions by which sulphuric acid is prepared in the leaden chamber.

3. How many tons of chamber vitriol, containing 70 per cent. of real acid (H_2SO_4) can be prepared from 250 tons of pyrites containing 42 per cent. of sulphur?

4. What is the composition of the crystals of the leaden chamber?

5. How many grams of oxygen can be obtained by the decomposition of 450 grams H_2SO_4 at a red heat?

6. Explain the action of phosphorous pentachloride on strong sulphuric acid.

7. How would you detect the presence of sulphuric acid?

8. What is the composition of sodium thiosulphate?

9. How is sulphuretted hydrogen prepared?

10. Explain how this gas may be used for the separation of the metals into groups.

11. Point out the relations existing between the oxygen and sulphur compounds.

12. What occurs when sulphur vapour is led over red-hot carbon, when H_2S is passed over red-hot platinum, and when ferrous sulphate is heated?

LESSON XIV. *Selenium, Tellurium, Silicon, and Boron.*

1. Mention the chief properties of selenium and tellurium.
2. In what respects does the element Se resemble S?
3. Trace the resemblances between the compounds of S, Se, and Te, with O and H respectively.
4. How is silicon prepared?
5. What names does the substance SiO_2 go by?
6. How can we obtain (1) soluble and (2) insoluble silica?
7. Explain the terms "dialysis," "colloid," and "crystalloid."
8. How is silicon tetrafluoride prepared?
9. How would you show that glass contains silica?
10. Where does boric acid occur?
11. What is the composition of borax?
12. How is boric acid prepared from borax? How much boron trioxide is contained in 3·82 grams of borax?

LESSON XV. *Phosphorus Compounds.*

1. Whence do animals ultimately get the phosphorus which they need?
2. How is phosphorus prepared from bone-ash?
3. Describe the different modifications of phosphorus?
4. How is white phosphorus transformed into red, and *vice versâ?*
5. What weight of phosphorus pentoxide can be obtained by burning one kilo. of phosphorus?
6. How is trihydrogen phosphate prepared?
7. Write down the formulæ of the tribasic sodium phosphates.
8. How many grams of sodium metaphosphate can be got by heating 100 grams of microcosmic salt?
9. How is metaphosphoric acid obtained, and how does it differ from phosphoric acid?
10. Write down the decomposition which occurs when we mix solutions of hydrogen di-sodium phosphate and silver nitrate ($AgNO_3$).
11. $4\ H_3PO_3 = 3\ H_3PO_4 + PH_3$. Describe this decomposition, and give the properties of the substances formed.
12. How are the chlorides of phosphorus prepared?

LESSON XVI. *Arsenic Compounds.*

1. How is arsenic separated from its ores?

2. Name the oxides of arsenic.

3. How does ferric hydrate act as an antidote to the poisonous properties of the arsenites and arsenates?

4. What is the composition and mode of preparation of arseniuretted hydrogen?

5. Name the tests by which arsenic can be detected with certainty.

6. Point out the general chemical relations of the arsenic, phosphorus, and nitrogen compounds.

LESSON XVII. *Atoms and Molecules.*

1. Define "atom" and "molecule," "atomic weight" and "molecular weight."

2. Given the density of any body volatile without decomposition, how can its molecular weight be found?

3. Explain fully what is meant when we say that chlorine is a *monad*, oxygen a *dyad*, nitrogen a *triad*, and carbon a *tetrad*.

4. Give examples of compound radicals belonging to the monad, dyad, and triad groups.

5. How is the *quantivalence* of an element or radical denoted?

6. Write down a series of decompositions in which the radical hydroxyl plays a part.

7. Why do elements act more energetically in the *nascent* state than in the ordinary condition?

8. State Avogadro's hypothesis, and the conclusions you draw from this as to the relation between vapour density and molecular weight of gaseous compounds.

9. Explain the action of ozone on hydrogen dioxide.

10. What is meant by valency of an element?

11. Can the same element possess different valencies? Give examples.

12. Explain by graphic formulæ the constitution of the oxy-acids of phosphorus.

LESSON XVIII. *The General Properties of the Metals.*

1. Name the metals which are lighter than water.

2. At what temperatures does mercury boil and freeze?

3. Describe the modes in which the metallic ores generally occur.
4. State some of the peculiar properties of the alloys.
5. Give an account of hydrogenium.
6. Under what classes may all the metals be arranged?
7. What is meant by a metallic salt?
8. Explain the relations existing between the atomic heats and combining weights of the elements.
9. State the law regulating the atomic heat of compounds.
10. Explain how the atomic heat of chlorine has been arrived at.
11. State how the metallic oxides are classified, and give illustrative examples.

LESSON XIX. *Crystallography.*

1. Give the chief characteristics of crystalline structure.
2. How is the cube derived from the regular octohedron?
3. Explain what is meant by the axes of a crystal.
4. What are the distinguishing characteristics of the six systems of crystallography?
5. How is the rhombohedron derived from the double six-sided pyramid?
6. Show how to distinguish between an octohedron, a quadratic pyramid, and an oblique pyramid.
7. What is the meaning of the terms isomorphism and dimorphism?

LESSON XX. *Metals of the Potassium Group.*

1. How was potassium first prepared, and how is it now manufactured?
2. State the sources of the potassium compounds.
3. How is caustic potash obtained?
4. Describe what happens when gunpowder is burnt.
5. Supposing that the decomposition is a simple one, how many cc. of (1) carbon dioxide and (2) of nitrogen gas at 0° and 760 mm. will be given off by burning one gram of English musketry powder?
6. Name the characteristic tests for potassium salts.
7. What are the sources of the sodium compounds?
8. Describe the salt-cake process.
9. How many tons of vitriol containing 72 per cent. of H_2SO_4 will be needed to convert 100 tons of salt into salt-cake, and how many tons of this latter will be formed?

10. How many tons of aqueous hydrochloric acid containing 30 per cent. of HCl will be formed in the preceding reaction?

11. Describe the decompositions by which salt-cake is converted into soda-ash.

12. Required 500 tons of soda crystals; what will be the weight of salt and pure sulphuric acid needed?

13. How were the two new alkali metals rubidium and cæsium discovered?

14. Explain the analogy in constitution existing between the potassium and ammonium salts.

15. How is hydroxylamine prepared, and what are its properties?

LESSON XXI. *Metals of the Alkaline Earths and of the Zinc Group.*

1. How can slaked lime be obtained from limestone, and what is its composition?

2. Describe the uses of lime in agriculture and the arts.

3. How can temporarily hard water be softened?

4. Name the commonest minerals containing barium and strontium.

5. How can oxygen gas be prepared from barium dioxide, and what process is employed for obtaining oxygen from the atmosphere in this way?

6. Mention the distinguishing reactions of the salts of barium, strontium, and calcium.

7. Describe how you would obtain a soluble salt of barium from the insoluble heavy spar.

8. Calculate the percentage composition of beryl.

9. Find the formula of a salt having the following percentage composition.

Magnesium	9·76
Sulphur	13·01
Oxygen	26·01
Water	51·22
	100·00

10. How can magnesium salts be distinguished and separated from those of calcium?

11. How is metallic magnesium obtained from magnesian limestone or dolomite?

12. What processes are used for extracting zinc from its ores?

13. In what respects do cadmium and the compounds of cadmium differ from those of zinc?

14. What tests would you employ to detect the presence of the compounds of zinc and cadmium?

LESSON XXII. *Metals of the Lead Group.*

1. Mention the decompositions which occur in the process of lead-smelting.

2. Under what circumstances may drinking water be contaminated with lead, and how would you show the presence of lead in such water?

3. Describe the oxides of lead. How is the dioxide obtained (*a*) from nitrate of lead, (*b*) from red lead?

4. What takes place when lead nitrate and lead dioxide are respectively heated? Give equations.

5. How is white lead manufactured?

6. 100 grams of lead oxide when reduced to the metallic state in a current of hydrogen lost 7·1724 grams. Calculate the combining weight of lead.

7. 4·9975 grams of lead chloride needed 3·881 grams of metallic silver for complete precipitation; required the atomic weight of lead, those of silver and chlorine being given.

8. What similarities are there between the compounds of lead and those of barium?

9. "The properties of thallium and its compounds are intermediate between those of lead and the alkalis," point out in detail facts bearing out this statement.

LESSON XXIII. *Metals of the Copper and Aluminium Group.*

1. How is copper obtained from copper pyrites?

2. Calculate the percentage of water contained in crystallized copper sulphate.

3. From cupric oxide how would you obtain (*a*) Scheele's green, (*b*) cuprous oxide, (*c*) metallic copper?

4. What is the density of mercury vapour? Does it obey the usual law of densities?

5. What weight of mercury and corrosive sublimate must be taken to yield three kilos. of calomel?

6. How is silver extracted from argentiferous lead?

7. 100 parts by weight of silver yield 132·84 parts of silver chloride. Given the atomic weight of chlorine calculate that of silver.

8. What decomposition does silver chloride undergo in the light?

9. Describe the electrotype process.

10. Give the characteristic reactions of copper, mercury, and silver salts.

11. Calculate the weight of metallic cerium contained in 10 grams of cerium potassium sulphate.

12. Find the percentage composition of potash alum.

13. How is metallic aluminium prepared?

14. Give a short account of the composition and properties of the different kinds of glass.

15. How are coloured glasses obtained?

16. How is common earthenware glazed?

17. Under what circumstances were gallium and indium discovered?

18. How would you show by chemical reactions that clay contains aluminium?

LESSON XXIV. *Metals of the Iron Group.*

1. State the composition of the several oxides of manganese.

2. How many liters of oxygen at 12° and under the pressure of 750 mm. can be got (*a*) by heating 500 grams of manganese dioxide, and (*b*) by treating the same weight of the same oxide with sulphuric acid?

3. How are potassium manganate and permanganate respectively obtained?

4. Mention some of the most important physical properties of iron.

5. How is ferrous sulphate obtained? Calculate the weight of crystals obtained by the slow oxidation of 230 tons of pyrites containing 37·5 per cent. of sulphur.

6. What is the composition of red hæmatite and of specular iron ore?

7. How can ferrous and ferric salts be distinguished?

8. Describe the manufacture of cast-iron from clay ironstone.

9. What chemical changes go on in the processes of "refining" and "puddling"?

10. How do cast-iron, steel, and wrought-iron differ in their composition?

11. Describe (*a*) the common method of making steel, (*b*) that known as the Bessemer method, (*c*) the basic method.

12. 3·285 grams of pure iron wire are burnt in excess (*a*) of

oxygen, (*b*) of chlorine; required the weight of oxide and of chloride formed.

13. What is the cause of the difference in the appearance and properties of "mottled" and "white" cast-iron?

14. In what minerals do cobalt and nickel occur, and how would you recognize these metals by the blowpipe?

15. What are the oxides of nickel and cobalt, and how are they obtained from the salts?

LESSON XXV. *Chromium, Molybdenum, Uranium, Tungsten, Tin, Titanium, Germanium.*

1. Give the names and formulæ of the oxides of chromium.

2. How can we pass from the sesquioxide to the trioxide and *vice versâ*?

3. Write down the formulæ of the potassium chromates.

4. What is the constitution and mode of preparation of chromium oxychloride?

5. How may chromic chloride be prepared?

6. What action has potassium bichromate on hydrochloric acid? Give equation.

7. How is molybdic acid obtained from the disulphide?

8. 4 grams of the disulphide gave 3·598 grams of the molybdic acid; calculate from these numbers the atomic weight of molybdenum.

9. Write down the principal oxides of uranium and compounds derived from them.

10. How is tungstic acid obtained from calcium tungstate, and how converted into the dioxide?

11. In what form does tin occur in nature, and how is metallic tin got from the ore?

12. What weight of crystallized "tin salts" can be prepared from one ton of metallic tin?

13. What are the characteristic reactions of tin?

14. In what respects do titanium and zirconium resemble tin?

LESSON XXVI. *Antimony, Bismuth, Vanadium, Gold, Platinum, and the rare Platinum-like Metals.*

1. Write down the names and formulæ of the oxides and sulphides of arsenic and antimony.

2. How does antimony differ from arsenic in its behaviour with chemical reagents?

3. Describe the preparation of the two chlorides of antimony.

4. How much manganese dioxide, salt, and sulphuric acid

will furnish chlorine enough to convert 100 grams of antimony into the trichloride?

5. Give equations for the reactions which take place when water is added to a solution of bismuth nitrate and of bismuth trichloride.

6. Draw up a comparison between the vanadium and phosphorus compounds.

7. How is gold transformed into the trichloride and into the trioxide?

8. How can spongy platinum be obtained from the tetrachloride, and how converted into coherent platinum?

LESSON XXVII. *Spectrum Analysis.*

1. Describe the phenomenon observed when a source of white light is examined by means of a prism.

2. What peculiarity is observed in the spectra of coloured flames?

3. How does the spectrum of a glowing solid differ from that of a glowing gas?

4. Mention some facts to show the extreme delicacy of the spectrum analytical methods.

5. How can the spectra of the metals be obtained?

6. Describe the construction and mode of use of the spectroscope.

7. Draw a rough sketch of the spectra of the following:—sodium, potassium, rubidium, lithium, and strontium (see Frontispiece).

8. Explain what is meant by Fraunhofer's lines.

9. Describe shortly an experiment to show the reversion of the bright line of sodium.

10. Why does Kirchhoff conclude that iron exists in the solar atmosphere?

11. How do we know that the fixed dark solar lines are not caused by absorption in the earth's atmosphere?

12. How can we learn the composition of the atmospheres of the fixed stars, and why are we in ignorance about the composition of the planets?

13. State the results of Mr. Huggins's observations upon the spectra of the nebulæ.

LESSON XXVIII. *Introduction to Organic Chemistry.*

1. Give a definition of an organic compound. In what respects does the class of organic compounds differ from the class of inorganic compounds?

2. Explain what is meant by the terms saturated and unsaturated compounds.

3. Give a definition or explanation of the terms, substitution product, additive product.

4. What is a homologous series, and what is the next higher homologue of the hydrocarbon ethane?

5. Show by means of formulæ how the ethyl compounds may be considered as derived from ethane.

6. What is meant by the term, organic radical; and by the same term when qualified by the words monatomic, diatomic, &c.?

7. What is an empirical and what a constitutional formula? Indicate briefly the way in which the empirical and the constitutional formulæ for a newly-discovered substance would be determined.

8. Define the term isomerism.

9. Given two organic compounds said to be isomeric how would you ascertain if this were so?

LESSON XXIX. *Organic Analysis, &c.*

1. Describe the processes adopted for the estimation of the carbon, hydrogen, nitrogen, and chlorine in organic compounds.

2. 0·3059 gram of a substance yielded on combustion 0·6000 gram carbon dioxide and 0·3040 gram water. Express its composition by the simplest formula possible.

3. From a monobasic acid its silver salt was prepared, analysed, and found to contain 53·6 per cent. of silver. What is the molecular weight of the acid?

4. 0·305 gram of a monobasic acid yielded on combustion 0·761 gram of carbon dioxide and 0·136 gram water; 0·301 gram of its silver salt contained 0·184 gram silver. Required the correct empirical formula of the acid.

5. Describe and explain a method for the determination of the vapour density of a substance. What is the use of the determination?

6. Required from the following numbers the vapour density of a hydrocarbon of the marsh-gas series: globe filled with air at 16°·5, 7·566 grams; filled with vapour at 140°, but weighed at 16°·5, 7·783 grams; capacity of globe 115·5 cc.

7. The vapour density of an alcohol was determined by Meyer's method: 0·120 gram expelled 49·3 cc. of air, the temperature of the air being 20°, and the height of the barometer 740 mm.

LESSON XXX. *Cyanogen, Carbonyl, and Thio-carbonyl Compounds.*

1. What is represented by the formulæ CN and C_2N_2? Compare the action of cyanogen and of chlorine on caustic soda solution.

2. Describe and explain the tests for hydrocyanic acid.

3. Describe the synthetical methods of preparing hydrocyanic acid.

4. What is a nitrile and why may hydrocyanic acid and cyanogen gas be called the nitriles of formic and of oxalic acids respectively?

5. How much potassium ferrocyanide, manganese dioxide, and ammonium sulphate should be required to prepare 500 grams urea?

6. Urea treated with sodium hypobromite solution containing caustic soda is decomposed: $CO(NH_2)_2 + 3NaOBr + 2\,NaOH = N_2 + 3\,NaBr + Na_2CO_3 + 3\ H_2O$; 50 grams of urine yielded on analysis 47·5 cc. of nitrogen at 11° and 754 mm. Required the percentage of urea contained.

7. Write the formulæ for ammonium carbonate, ammonium carbamate and carbamide.

8. Compare the action of a dilute acid on potassium cyanate and thiocyanate.

LESSON XXXI. *Paraffin Group and Methyl Series.*

1. Define the term paraffin. Compare the percentage compositions of (1) the second and third, and (2) the thirty-second and thirty-third members of the paraffins.

2. Write the constitutional formulæ for all possible isomerides of pentane.

3. What products are obtained by the action of dilute chromic acid solution, or of dilute sulphuric acid and manganese dioxide on a primary alcohol?

4. Write the formulæ for ethyl hydroxide, oxide, chloride, and amide: compare the corresponding acetyl compounds; give the substances their common names.

5. Given two samples, one primary propyl alcohol, the other secondary propyl alcohol, how would you ascertain (1) physically, (2) chemically, which was which?

6. Write the constitutional formulæ for carbinol, dimethyl-carbinol, ethyl-carbinol, trimethyl-carbinol.

7. By what reactions are we enabled to pass from the methyl to the ethyl series?

8. Why is methyl-carbamine written $CH_3.NC$ and acetonitrile $CH_3.CN$?

LESSON XXXII. *Dicarbon or Ethyl Series, and Higher Carbon Series.*

1. Given carbon, hydrogen, oxygen, sulphur, and any other elements, how may alcohol be prepared?

2 Ethyl alcohol is isomeric with methyl ether; how has the constitution of these two bodies being determined?

3. The specific gravity of beer cannot be used as a test of the amount of alcohol present. Why? What method would you propose for this determination?

4. When alcohol and strong sulphuric acid are mixed the reaction is never complete. What acid is formed, and how may its potassium salt be prepared in a state of purity? Barium ethyl sulphate is readily soluble in water.

5. Compare the preparation of hydrobromic acid from phosphorus, bromine and water, with the preparation of ethyl bromide from phosphorus, bromine and alcohol.

6. How do we know that the four carbon atoms in ethyl ether are not all directly connected together? Explain the continuous etherification process.

7. In what manner is it shown that in nitrile the carbon atom, and not the nitrogen atom, of the cyanogen group is attached to the alcoholic radical?

8. What materials are required to convert ethyl alcohol into propionic acid?

9. How many grams of ethylamine can be prepared from 100 of ethyl carbimide?

10. Ethyl cyanate is written C_2H_5OCN and ethyl carbimide $C_2H_5.NCO$. Why is this?

11. Write out in full the constitutional formulæ for isobutyl carbinol and secondary butyl carbinol.

12. How many hexanes can exist? Give their constitutional formulæ.

LESSON XXXIII. *Compounds derived by Oxidation from the Alcohols.*

1. Mention the chief reactions by which the fatty acids can be formed.

2. How many grams of potassium formate can be got from 500 liters of carbon monoxide at 15° and 745 mm.?

3. Required 100 kilos. of CH_2O_2; how many kilos. of oxalic acid are needed?

4. What is the formula of formamide?

5. How can acetaldehyde be produced from acetic acid, and how can aldehyde be reduced to alcohol?

6. Explain what is meant by acetous fermentation.

7. What is the composition of red and iron liquors?

8. How many grams of glacial acetic acid can be obtained from 25 kilos. of potassium acetate?

9. How is acetyl oxide (acetic anhydride) prepared?

10. Name some of the chlorine substitution-products of acetic acid.

11. Give the formulæ and mode of preparation of thiacetic acid, acetyl peroxide, acetamide, acetone, acetylene.

12. Show that by substituting hydrogen in the radical of acetic acid, by methyl and ethyl we obtain (1) propionic and (2) butyric acids.

13. Describe the constitution of the isomeric alcohols, acids, and hydrocarbons of the 4-carbon series.

14. Point out several methods by which we can pass from the di- to the tri-carbon series.

LESSON XXXIV. *Compounds of the Alcohol Radicals with the Elements of the Nitrogen Group.*

1. Required the percentage of platinum contained in $[N(C_2H_5)_3]_2H_2PtCl_6$.

2. What are the molecular weight and possible formulæ of a double platinum salt yielding on heating 29·4 per cent. of metallic platinum?

3. Explain the meaning of the terms primary, secondary, and tertiary when applied (1) to amines, (2) to alcohols.

4. How would you determine the constitution of a compound ammonia of the composition C_3H_9N; how many isomerides are possible?

5. What bodies are obtained by the action of ethyl iodide on zinc; and (2) on zinc and water; (3) zinc and hydrochloric acid?

6. Express by equation the action of arsenic trioxide on heated sodium acetate.

7. Describe all the steps necessary to convert ethyl alcohol into propionic acid, passing through zinc ethyl.

LESSON XXXV. *Divalent Alcohols.*

1. What is meant by a divalent alcohol?
2. Mention the chlorine substitution-products of ethylene.
3. Why is ethylene regarded as an unsaturated compound?
4. How is glycol prepared?
5. What are the products of oxidation of glycol?
6. How is ethylene oxide distinguished from aldehyde?
7. Describe the difference in constitution between the ethylene and ethidene series of compounds.
8. How many grams of oxygen are required to burn completely 100 grams of trimethylene glycol?
9. Write down a list of the olefines with their formulæ.
10. What is the name of $C_6H_{12}(OH)_2$?
11. Write out the formulæ of some ethylene diamines.

LESSON XXXVI. *Divalent Acids.*

1. How are the acids of (1) the lactic series, and (2) of the oxalic series, derived from the corresponding glycols?
2. Show that hydroxycarbonic acid is the first term of the first series.
3. Write the formula of dimethyl thiocarbonate.
4. How many grams of oxygen are required to oxidize 100 grams of glycollic to oxalic acid?
5. How can oxalic acid be obtained from carbon, oxygen, and sodium?
6. Describe the manufacture of oxalic acid from sawdust.
7. Show that lactic acid can be formed from chloropropionic acid.
8. In what important respect, as regards the formation of salts, do lactic acid and its homologues differ from oxalic acid and the higher terms of its series?
9. Distinguish between ordinary lactic acid and ethylene lactic acid.
10. Explain the reaction—

$$C_3H_4(CN)_2 + 4H_2O = C_4H_6O_4 + 2NH_3.$$

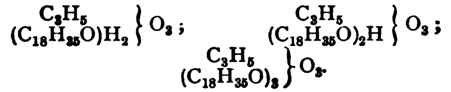
11. How can malic and tartaric acids be obtained from succinic acid?
12. Describe the several varieties of tartaric acid.
13. What is the action of hydriodic acid upon tartaric acid?

LESSON XXXVII. *Trivalent and Hexavalent Alcohols. Allyl Group.*

1. Show the relation in composition existing between propyl alcohol, propylene glycol, and glycerol.

2. Explain the process of saponification.

3. Explain by formulæ the composition of the chlor hydrins.

4. 

$$\left.\begin{matrix}C_3H_5\\(C_{18}H_{35}O)H_2\end{matrix}\right\}O_3;\qquad \left.\begin{matrix}C_3H_5\\(C_{18}H_{35}O)_2H\end{matrix}\right\}O_3;$$

$$\left.\begin{matrix}C_3H_5\\(C_{18}H_{35}O)_3\end{matrix}\right\}O_3.$$

Name the above bodies.

5. How is allyl alcohol prepared from glycerol.

6. What is the composition of acroleïn?

7. What is the constitution of mannitol; and what reasons have we for supposing it to be hexavalent alcohol?

8. Explain the following:

$$C_6H_{14}O_6 + 11HI = C_6H_{13}I + 6H_2O + 5I_2.$$

LESSON XXXVIII. *Carbohydrates.*

1. Give a short description of the preparation and refining of cane sugar.

2. Write down the formulæ of saccharoses and hexoses.

3. What is meant by right- and left-handed rotatory power?

4. What is the action of yeast and dilute sulphuric acid upon cane sugar?

5. How is glucose prepared?

6. By what formulæ are the differences between glucose and fructose expressed?

7. Give a short account of the principal phenomena of fermentation.

8. How does starch differ in constitution from glucose?

9. What weight of dextrin and dextrose can be obtained from 1 kilo. of starch by the action of diastase?

10. What is the composition of gun-cotton, and what advantages does it offer over gunpowder?

LESSON XXXIX. *Group of Aromatic Compounds.*

1. How do we suppose the carbon atoms in benzene are arranged? Give proofs of formula.

2. Write down the formulæ for benzene, phenol, aniline, toluene.

3. How many di- and tri-substitution products of benzene can be formed?

4. Explain the meaning of the terms ortho, meta, and para series, as applied to the dimethyl-benzenes.

5. What substances are formed by the replacement of one atom of hydrogen in benzene by NO_2, NH_2, and OH? Describe their method of preparation and properties.

6. Describe the methods employed for converting aniline into benzene, phenol, and bromobenzene.

7. Required the volumes at 0° and 760 mn. of nitrogen and carbon dioxide obtained by the combustion of 216 grams of aniline.

8. Explain the action of nitrous acid on aniline nitrate.

9. How can oil of bitter almonds be converted into benzoic acid, and *vice versâ?*

10. Explain the constitution of toluidine and benzylamine.

11. Explain the following:

$$\left.\begin{array}{r}C_7H_5O\\K\end{array}\right\}O + C_7H_5OCl = \left.\begin{array}{c}C_7H_5O\\C_7H_5O\end{array}\right\}O + KCl.$$

12. How is rosaniline prepared?

13. Explain the relation of leucaniline to rosaniline, and of white to blue indigo.

14. State the relation of naphthalene and anthracene to benzene.

15. What is the chief colouring matter of madder? and how can it be artificially prepared?

16. How can indigo be prepared artificially?

LESSON XL. *Terpenes, Camphor, and the Glucosides.*

1. What are the chief sources of the essential oils?

2. What is the composition of the terpenes, and with what aromatic hydrocarbon are they closely allied?

3. Name the chief constituent of oil of turpentine; what is its action on the plane of polarized light?

4. Give the source and chief properties of camphor.

5. What is the relation between limonene and dipentene?
6. What is the chemical nature of the glucosides; how have they been artificially prepared?

LESSON XLI. *The Alkaloids.*

1. From what substances are the alkaloids mostly derived, and in what relationship do these stand to benzene and naphthalene?
2. How is piperidine prepared?
3. Describe the synthesis of coniine.
4. What are the chief alkaloids contained in opium?
5. Find the molecular weight of an alkaloid whose monohydrochloride contains 11 per cent. of chlorine.
6. From what substances is antipyrine prepared; what is its most remarkable property?

LESSON XLII. *Albuminous Substances.*

1. In what chemical characters do the albuminous bodies differ from definite chemical compounds?
2. How may fibrin, albumin, and caseïn be separated?
3. Describe shortly the composition and properties of blood, milk, and bile.
4. Distinguish between animal and vegetable life.
5. What is the result of work and rest upon the excretion of carbon dioxide and the absorption of oxygen in the body?
6. From what source do animals obtain the energy necessary for existence? and whence do plants draw the energy needed for the organization of their food?

LESSON XLIII, *Organic Synthesis.*

1. By what experiment was the belief in the so-called vital force first shaken?
2. How may formic and oxalic acids be obtained from their elements?
3. Describe the synthesis of fatty acids and ketones from acetoacetic ether.
4. In what manner has citric acid been obtained artificially?
5. From what natural source is salicylic acid obtained, and how is it prepared synthetically?

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